APPENDIX A

ENVIRONMENTAL STANDARDS INC.

DATA VALIDATION

STANDARD OPERATING PROCEDURES

MERCURY BY SW-846 METHODS

I. Introduction

This Standard Operating Procedure addresses the data validation procedures for the review of data for the analysis of aqueous and solid samples by SW-846 methods 7470A and 7471A. These methods are cold-vapor atomic absorption procedures. Samples must be digested prior to analysis. Mercury is reduced to the elemental state through digestion. High concentrations of sulfides and copper can interfere with the analysis for mercury. High concentrations of chlorides in samples may require extra potassium permanganate to reduce possible interferences. Certain volatile organics that absorb 253.7 nm wavelength also interfere with the analysis.

II. Contractual Holding Times and Sample Preparation

A. Review Items:

Form I's, Form XIIIs, Form XIVs, Chain-of-Custody forms, digestion logs, Case Narratives, and microwave calibration (if microwave digestion performed).

B. Evaluation Procedure:

Contractual holding times are established by comparing the dates of sample receipt on the Chain-of-Custody forms with the dates of sample receipt and analysis on the Form I's, Form XIIIs, Form XIVs, and the raw data. Examine the sample records (i.e., digestion logs) to determine if samples were preserved.

C. Criteria:

1. Contractual holding times (from date of sample receipt) and required preservation for mercury:

Aqueous samples:	28 days; preserved to pH <2 with HNO3
Solid samples:	28 days; cool to 4±2 C°

2. Mercury digestion involves 100 mL initial volume to 100 mL final volume for aqueous samples and either three 0.2 gm aliquots or one 0.6 gram aliquot initial sample weight to 100 mL final volume for soils.

D. Actions:

1. If the Case Narrative, Chains-of-Custody or digestion logs are not included in the data package, a correctable deficiency should be written in the quality assurance review. If necessary, and if time permits, contact laboratory and/or client for resubmissions.

2. If the date of sample receipt is not recorded on the Chain-of-Custody, a noncorrectable deficiency should be written in the quality assurance review. Contact the laboratory to determine the date of sample receipt. If the date of sample receipt is not recorded, assume the date to be the day after sample collection.

3. If contractual holding times have been exceeded, a noncorrectable deficiency should be written in the quality assurance review.

4. One digestion is allowable for microwave digestion for aqueous samples. Two digestions must be performed for soils by hot plate, soils by microwave, and aqueous by hot plate.

5. If correct weights/volumes are not used in the digestion, a noncorrectable deficiency should be written in the quality assurance review.

6. If the aqueous pH is >2 for mercury, add a paragraph to this effect to the "Noncorrectable Deficiencies" section of the quality assurance review.

7. If inconsistencies are discovered between the Form XIIIs and the sample digestion logs, a correctable deficiency should be noted in the quality assurance review. Contact the laboratory to verify sample digestion volumes/weights if necessary.

8. If the pH of an aqueous sample is >2 but <6, flag all positive results for mercury "J" and "not-detected" results for mercury "UJ" ("UL" for Region III).

9. If the pH of a sample is >6 for the mercury analysis, flag positive results for mercury "J" and flag "not-detected" results for mercury "R."

10. Client should be informed immediately (via telephone) if the pH is not appropriate.

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11. If samples are analyzed outside of holding times, flag all positive results for mercury "J" and "not-detected" results for mercury "UJ" ("UL" for Region III) for the samples. If the holding times are grossly exceeded, flag positive results for mercury "J" and flag "not-detected" results for mercury "R." Holding times are considered to be grossly exceeded if a sample analysis exceeds 2× the technical holding time.

12. If the temperature of samples received at the laboratory exceeds 6.0°C, the reviewer should attempt to ascertain how the temperature was obtained and if all NIST calibration correction factors were applied. A comment relating to both issues should be included with any qualifier. For all samples, temperatures greater than 6°C but ≤10°C for mercury will result in flagging positive results for mercury "J" and not-detected results "UJ" ("UL" for Region III). For "not-detected" mercury results with temperatures >10°C, flag the data "R." For all mercury analyses, the Federal Register specifies HNO_3 preservation (aqueous only) with no requirement for 4±2°C.

III. Calibrations and CRA Standards

A. Review Items:

Form II's, Form XIVs, and raw calibration data.

B. Evaluation Procedure:

1. Verify that the instrument was calibrated daily (within 24-hour period) and each time the instrument was set up using the correct number of standards and a blank.

2. Verify that the daily calibrations meet the required criteria. In addition, verify that the ICV was analyzed <u>immediately</u> <u>after</u> the daily calibrations.

3. Verify that a standard at the quantitation/reporting limit was used in all calibration curves.

4. Verify that all ICV and CCV recoveries fall within the required recovery ranges.

5. Check the raw data to verify that the calibration standard values were transcribed correctly onto Form II's (check all values). Recalculate the ICV

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and CCV percent recoveries (%R) and verify that the recalculated value agrees with the laboratory-reported values on the Form II's.

6. Verify that a CCV was analyzed before and after all analytical samples are analyzed and after every 10 analytical samples or every 2 hours, whichever is more frequent. This can be accomplished by examining the raw data and indicating the times of analysis on the Form IIAs or using the Form XIVs in conjunction with the raw data.

7. Verify that a standard (defined as CRA) at the quantitation/reporting limit was analyzed to verify linearity near quantitation/reporting limit. The CRA should be analyzed before all samples are analyzed but not before the ICV and ICB.

C. Criteria:

1. Initial Calibration:

Instruments must be calibrated daily and each time the instrument is set up. A blank and at least four standards, one of which should be at the quantitation/reporting, must be used in establishing the analytical curve.

2. Initial and Continuing Calibration Verification (ICV and CCV); CRA:

Analysis results for mercury must fall within the control limits of 80-120%. If ICV/CCV fails criteria, all samples up to the previous acceptable CCV must be reanalyzed. It is preferable that the Initial Calibration Verification (ICV) standard have a concentration different from that used for initial standardization of the instrument.

a. The ICV must be analyzed immediately after the daily calibrations. A CCV should be analyzed after every ten analytical samples or every 2 hours, whichever is more frequent, prior to sample analysis, and at the end of the analytical sequence. Note that the concentration of the CCV does not necessarily have to be different than that of the ICV. The CCV should be at a concentration at or near the mid-range of the calibration curve.

b. To verify linearity near the quantitation/reporting limit, the laboratory should analyze a standard at the quantitation/reporting limit (called the CRA standard). The CRA standard should be analyzed before all samples have been analyzed.

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c. For mercury analyses, calibration standards should be prepared at the time of analysis. The time and date of standard preparation and analysis should be documented in the raw data.

d. Analysis results for the ICV/CCV and ICB/CCBs must be reported on the Form IIs in the order in which the standards were run.

e. Baseline correction is acceptable if it is performed after every sample or after every CCV and CCB analysis. Resloping the instrument is acceptable as long as it is immediately preceded by and immediately followed by compliant CCVs and CCBs.

D. Actions

1. If the instrument used for sample analysis was not calibrated at the proper frequency or was not performed using the correct number of standards and blanks, a noncorrectable deficiency should be written in the quality assurance review.

2. If any of the raw data for the initial calibration, the CRA, the initial calibration verification or continuing calibration verifications or if the Form IIs are not included in the data package received, a correctable deficiency should be written in the quality assurance review. If necessary, contact the laboratory and/or client for submission of missing items.

3. If an EPA-certified standard was not used for the ICV and the laboratory did not use a separate source and different concentration (other than what was used for calibration) for the ICV, a noncorrectable deficiency should be written in the quality assurance review.

4. If the recovery of an analyte in an ICV or CCV falls outside the required recovery criterion, and the laboratory did not terminate the analysis, recalibrate and reanalyze all associated samples back to the last compliant CCV, a noncorrectable deficiency should be written in the quality assurance review. Note in the deficiency whether the data usability of the associated samples was affected or not.

5. If the concentration or recovery of an analyte in an ICV or CCV (or the CRA) was misreported on a Form II, then a correctable deficiency should be written in the quality assurance review.

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6. If an ICV and/or CCV were not analyzed at the proper frequency or in the appropriate sequence, then a noncorrectable deficiency should be written in the quality assurance review. Note: the time between any CCV analysis and either the analytical sample before or the CCB after should not be any longer than the time between any two consecutive analytical samples.

7. If a CRA standard was not analyzed at the appropriate concentration, in the appropriate sequence, or at the appropriate frequency, a noncorrectable deficiency should be written in the quality assurance review.

8. If a calibration standard with a concentration at the CRA was not analyzed as part of the initial calibration for mercury analyses, then a noncorrectable deficiency should be included in the quality assurance review.

9. If the calibration standards for mercury were not prepared at the time of analysis, then a noncorrectable deficiency should be included in the quality assurance review. In addition, if the time and date of standard preparation is not in the raw data, a correctable deficiency should be written in the quality assurance review.

10. If the results of the ICV/CCV and ICB/CCB analyses were not reported in the proper (temporal) order, include a correctable deficiency in the quality assurance review.

11. If the raw data show that the ICV was not analyzed immediately after the daily calibration, include a noncorrectable deficiency in the quality assurance review.

12. If the correlation coefficient is <0.995 and a straight line curve in being used for calibration, qualify results >IDL as estimated ("J"), and "not-detects" as "UJ."

13. If the ICV or CCV %R falls outside the acceptance windows, qualify according to the following. The qualification should be applicable to the preceding samples and the samples following the recovery for the CCV out of criterion. If the ICV is out of criterion, the entire sequence would be qualified. The following are policy by Region II and recommended by Region I and the Functional Guidelines. Qualify only samples before and after CCVs with poor recoveries. If the ICV is outside criterion, qualify the samples of the entire analytical sequence.

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a. If the ICV or CCV %R falls outside the acceptance windows but within the ranges of 65-79% or 121-135%, qualify results >quantitation limit/reporting limit as estimated ("J").

b. If the ICV or CCV %R is within the range of 121-135%, results <IDL are acceptable.

c. If the ICV or CCV %R is 65-79%, qualify results <IDL as estimated ("UJ", "UL" for Region III).

d. If the ICV or CCV %R is <65%, qualify all positive results and quantitation limits/reporting limits as unusable ("R"). In the narrative, discuss the probability of positive results being qualitatively valid but quantitatively biased very low.

e. If the ICV or CCV %R is >135%, qualify results >IDL as unusable ("R"); results <IDL are acceptable.

14. Per Region II, if a continuing calibration verification was not performed at the proper frequency, all applicable results should be flagged "J" and "not-detects" flagged "UJ."

15. Per Region II, if the recoveries of the CRA are outside 80-120%, then qualify according to the following guidelines. Note that the qualification is only applicable to samples analyzed in the affected sequence.

a. If the recovery is between 50-79%, flag all positive results "J" and "not-detected" results "UJ."

b. If the recovery is between 121-150%, flag all positive results "J."

c. If the recovery is <50%, flag all results "R." However, for positive results, note in the report that the presence is qualitatively valid, but the reported results are quantitatively biased quite low.

d. If the recovery is >150%, flag all positive results "R."

16. Per Region I, if the recoveries of the CRA standard are outside 80-120%, then flag positive results < 3× quantitation limit/reporting limit "J" and "not-detects" "UJ." Do <u>not</u> qualify data >3× quantitation limit/reporting limit.

17. Per Region III, if the recoveries of the CRA are outside 90-110%, then qualify according to the following guidelines. Note that the qualification is only applicable to samples analyzed in the affected sequence.

    a. If the recovery is between 50-89%, flag all positive results reported at less than 2× the quantitation limit/reporting limit "J" and "not-detected" results "UL."

    b. If the recovery is greater than 110%, flag all positive results reported at levels less than 2× quantitation limit/reporting limit "J."

    c. If the recovery is <50%, flag all "not-detected" results "R" and all positive results reported at levels less than 2× quantitation limit/reporting limit "J." However, for positive results, note in the report that the presence is qualitatively valid, but the reported results are quantitatively biased quite low.

18. Environmental Standards, Inc. Policy:

    a. Apply the following criteria to results <2× quantitation limit/reporting limit for mercury and <3× quantitation limit/reporting limit for all others. Do <u>not</u> apply the criteria to results obtained by the method of standard additions.

    b. When following the Functional Guidelines, there is no policy for CRA recoveries. In this case, data will be qualified according to the following:

        i. If the recovery is between 50-75.0% for mercury, flag positive results "J" and "not-detected" results "UJ."

        ii. If the recovery is between 125.1-150% for mercury, flag positive results "J."

        iii. If the recovery is <50%, flag positive results "J" and "not-detected" results "R."

        iv. If the recovery is >150%, flag positive results less than 3× quantitation limit/reporting limit "R." For results equal to or greater than 3× quantitation limit/reporting limit and less than

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5× the quantitation limit/reporting limit, flag positive results "J."

NOTE: In all cases above if the IDL is greater than the quantitation limit/reporting limit, replace "quantitation limit/reporting limit" with "IDL."

IV. Blanks

A. Review Items:

Form IIIs, raw data, and digestion logs.

B. Evaluation Procedure:

1. Review the results reported on the Form IIIs, as well as the raw data for all blanks, and verify that the results were accurately reported.

2. Verify that the calibration blanks and preparation blanks were analyzed in the proper order and at the proper frequency.

3. Verify that the absolute value of the concentration of an analyte detected in a blank does not exceed the quantitation/reporting limit.

4. Verify that all blank results at or above the quantitation/reporting limit are reported on the Form III.

C. Criteria:

1. The magnitude (absolute value) of a calibration blank (ICB or CCB) result must not exceed the quantitation/reporting limit. If it does, the analysis must be terminated, the instrument recalibrated and the preceding analytical samples must be reanalyzed.

2. The concentration (absolute value) of a preparation blank (PBS [for solids] or PBW [for aqueous]) must not exceed the quantitation/reporting limit. If it does, all associated samples reported below 10× the blank concentration but greater than the quantitation/reporting limit associated with the blank must be redigested and reanalyzed. If the blank concentration is less than the negative quantitation/reporting limit, all associated samples reported below 10° the CRDL must be redigested and reanalyzed. Check the digestion logs to determine which samples are associated with the preparation blank.

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2. A preparation blank must be analyzed for each matrix, for every 20 samples digested, or for each batch digested, whichever is more frequent. Note that an aqueous preparation blank must be digested and analyzed even if the only aqueous samples in the batch are field blanks.

3. Calibration blanks (ICB and CCB) must be analyzed immediately after every initial (ICB only) and continuing calibration verification (CCB only) at a frequency of every ten samples or every 2 hours (CCB only), whichever is more frequent.

D. Actions:

1. If a preparation blank or calibration blank was not analyzed at the proper frequency and/or sequence, then a noncorrectable deficiency should be written in the quality assurance review.

2. If the results for a blank were misreported on a Form III, a correctable deficiency should be included in the quality assurance review.

3. If the magnitude (absolute value) of an ICB, CCB or preparation blank result exceeds the quantitation reporting limit without corrective action being taken, a noncorrectable deficiency should be written in the quality assurance review.

4. Note that ICB, CCB, and aqueous preparation blanks are always in units of µg/L and preparation blanks for solids are to be reported in mg/Kg. If these units were not used, a correctable deficiency should be included in the quality assurance review.

5. In instances where more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration of a contaminant. The result must not be corrected by subtracting any blank value. Action levels should be calculated that are five times the maximum concentration of each contaminant detected in any blank. No positive results should be reported unqualified unless the concentration of the analyte in the sample exceeds 5 times the amount detected in any blank.

NOTE: The reviewer should note that the blank analyses may not involve the same weights, volumes, or dilution factors as the associated samples. In particular, solid sample results reported on the Form I's will not be on the same bases (units, dilutions) as the calibration blank data reported on the Form IIIs. Sample weights,

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volumes, and dilution factors must be taken into consideration on a sample-specific basis when applying the 5× criteria.

6. The results of all initial calibration blanks, continuing calibration blanks, and preparation blanks should be applied to all samples in the SDG.

7. Results of the field blanks should be applied to all samples collected on the same day. However, consideration should be given to the samples with which the field blank was prepared (digested).

8. Sample results should be reported as follows:

   a. If mercury is detected in the blank but not in the sample, no action is taken.

   b. Positive results less than the action level shall be reported with a "U" (except for Region III, where results should be flagged "B").

   c. Positive results greater than the action level shall be reported unqualified with respect to blank results only.

   d. Per Region II, if an analyte cannot be qualitatively questioned due to its presence in a laboratory blank but can be questioned due to its presence in a field blank, all positive sample results ≤5× the value in the field blank should be flagged "R." (Note that Region II specifies using blanks that are ≥ quantitation limit/reporting limit; Environmental Standard's policy is to use blank results ≥ the IDL, regardless of Region II guidelines.)

   e. Per Region III, if any blank has a negative result whose absolute value is greater than the quantitation limit/reporting limit, then all samples associated with the blank should be qualified as "J" for positive results reported at levels less than 5× quantitation limit/reporting limit and "UL" for "not-detected" results.

V. Laboratory Control Sample Analysis (LCS)

A. Review Items:

Form VIIs, raw data, and digestion logs.

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B. Evaluation Procedure:

1. Review Form VIIs and verify that results fall within the control limits.

2. Review digestion logs and verify that the LCS was digested.

3. Check the raw data to verify reported results on Form VIIs. Recalculate the recoveries for all LCS results for mercury.

4. Verify that all LCS were analyzed at the proper frequency.

C. Criteria:

1. An LCS must be analyzed for each analyte using the same sample preparations and methods employed for the samples received. An LCS must be prepared and analyzed per matrix and per SDG or digestion/distillation batch (whichever is more frequent). If the aqueous LCS is not available from the EPA, the ICV standard can be used as the LCS.

2. All aqueous LCS results must fall within the control limits of 80-120%.

3. All solid LCS results must fall within the control limits established by the EPA.

D. Actions:

1. If the LCS analyses are not run at the proper frequency or were not digested, a noncorrectable deficiency should be written in the quality assurance review.

If the results for the LCS analyses are not reported or are misreported on the Form VIIs, a correctable deficiency should be written in the quality assurance review.

3. If the results for an LCS fall outside the specified control limits and samples are not redigested for the applicable analytes, then a noncorrectable deficiency should be written in the quality assurance review.

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4. Aqueous LCS:

   a. If the LCS recovery for any analyte falls within the range of 50-79% or 120-150%, qualify results >IDL as estimated ("J"). However, positive results for analytes displaying recoveries >150% should be flagged "R."

   b. If results are <IDL and the LCS recovery is greater than 120%, the data are acceptable.

   c. If results are <IDL and the LCS recovery falls within the range of 50-79%, qualify the data for these samples as estimated ("UJ" or "UL").

   d. If LCS recovery results are <50%, qualify the data for these samples as unusable ("R").

5. Solid LCS:

   a. If the solid LCS concentration for any analyte falls outside the EPA control limits, qualify all sample results >IDL as estimated ("J"). Region II makes an exception for analytes with an IDL ≥ true value of the LCS.

   b. If the LCS results are higher than the control limits and the sample results are <IDL, the data are acceptable.

   c. If the LCS results are lower than the control limits, qualify all sample results <IDL as estimated ("UJ"; "UL" for Region III). Region II makes an exception for analytes with an IDL ≥ true value of the LCS.

   d. Environmental Standards Policy: For solid LCSs, recoveries outside the 70-130% range shall require qualification. Positive results are flagged "J"; "not-detected" results associated with solid LCS recoveries <70% are flagged "UJ" ("UL" for Region III). The only exception is when the true value is below <3× the IDL or the quantitation limit/reporting limit (whichever is lower), in which case no qualification is warranted from a recovery perspective.

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6. Per Region II, if an LCS analysis was not performed at the proper frequency, all positive results should be flagged "J" and "not-detects" should be flagged "UJ." See additional requirements in the Region II SOP.

VI. Duplicate Sample Analysis

A. Review Items:

Form VIs, Form I's, and raw data.

B. Evaluation Procedure:

1. Review Form I's and Form VIs and verify that results either fall within the control limits or have been flagged with an "*" on the Form I's and Form VIs (of similar matrix). Verify that all control limits (dry-weight corrected for solids) are specified on the Form VI for those analytes above the quantitation/reporting limit in either the initial or the duplicate determinations. The control limit is not required if both analytical results are either <quantitation/reporting limit or >5× quantitation/reporting limit.

2. Check the raw data and recalculate the RPDs to verify that results have been correctly reported on the Form VI. Note that duplicates are also required for percent solids but the duplicate sample results should be calculated from the initial percent solids determination. When a sample result is less than the quantitation/reporting limit, consider the result to be zero in calculating the RPD.

3. Verify that the field blank was not used for duplicate analysis.

4. Verify that duplicates were prepared at the required frequency.

5. For solid samples, verify that the laboratory used the percent solids for the original sample to calculate the results for the analytes in the duplicate sample.

C. Criteria:

1. A duplicate sample must be prepared and analyzed for every 20 samples, for each procedure used to report analytical results, or for every matrix, whichever is more frequent.

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2. Samples identified as field blanks should not be used for duplicate sample analysis.

3. A control limit of 20% for RPD is used for aqueous samples and duplicate results greater than 5x quantitation/reporting limit (40% RPD for solid samples; the laboratory should report these on a dry-weight basis).

4. A control limit of ± quantitation/reporting limit is used for sample and/or duplicate results less than 5x quantitation/reporting limit (±2× quantitation/reporting limit for solid samples).

5. The laboratory must perform and report the results of a duplicate percent solids analysis. However, the reported results for the duplicate sample on the Form VI must be calculated using the percent solids for the original sample (the percent solids reported on the Form I for the original sample).

D. Actions:

1. If duplicate analysis results for a particular analyte fall outside the appropriate control limits and the results have not been flagged with an "*" on the Form VI and all associated Form I's (for that matrix), then a correctable deficiency should be written in the quality assurance review.

2. If there are any discrepancies between the raw data, Form VIs, Form I's or RPD calculations or if there are any missing control limits, a correctable deficiency should be written in the quality assurance review.

3. If the field blank was used for duplicate analysis, a noncorrectable deficiency should be written in the quality assurance review.

4. If a duplicate sample analysis was not performed at the proper frequency, a noncorrectable deficiency should be written in the quality assurance review.

5. If the laboratory did not report a control limit when one or both of the sample results was greater than the quantitation/reporting limit but less than 5× quantitation/reporting limit, include a correctable deficiency in the quality assurance review.

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6. If the laboratory used the results of the duplicate percent solids determination (rather than the percent solids of the original sample) to calculate the results for the solid sample duplicate analysis, include a correctable deficiency in the quality assurance review.

Note: The following actions apply to samples associated with the laboratory duplicate sample. In most cases, a laboratory will analyze one duplicate sample for each matrix in an SDG. However, there may be times when more than one duplicate analysis is performed for a given matrix in an SDG. In these cases, use the digestion logs provided to associate samples with the laboratory duplicate sample analyses.

7. Per Region I and the Functional Guidelines, if duplicate analysis results for a particular analyte fall outside the appropriate control windows, qualify the positive results for that analyte in all samples of the same matrix as estimated ("J"). If one result is less than the IDL, use a value of the IDL for that result for comparison only. Consider a result real if qualified "B" (i.e., use the reported concentrations).

8. Per Region II, if the RPD is >50% (when sample and duplicate are ≥ 5× quantitation limit/reporting limit), or the difference between sample and duplicate > quantitation limit/reporting limit (when sample and/or duplicate are <5× quantitation limit/reporting limit), flag all positive results "J" for aqueous samples. It is Environmental Standards' policy to qualify positive results "J" for aqueous samples if the RPD is greater than 20% regardless of Region II SOP.

9. Per Region II, if the RPD is >100% (when sample and duplicate are ≥ 5× the quantitation/reporting limit) or the difference between sample and duplicate > quantitation/reporting limit (when sample and/or duplicate are < the quantitation/reporting limit), flag all positive results "J" for solid samples. It is Environmental Standards' policy to qualify positive results "J" for soil samples if the RPD is greater than 35%, regardless of the Region II SOP.

10. Per Region II, if one value for a sample duplicate pair is < the quantitation/reporting limit and the other is ≥ 10× the quantitation/reporting limit, all positive results should be flagged "R".

11. Per Region II, if a field blank was used for the laboratory duplicate analysis, all associated positive results > the quantitation/reporting limit should be

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flagged "J" except in the case where the field blank is the only aqueous sample in the SDG.

12. Refer to Region II SOP for additional guidance.

13. When evaluating laboratory duplicate results, keep in mind the analyte concentrations in the method blanks. It may be possible in some instances to attribute high imprecision to blank contamination.

VII. Matrix Spike Analysis

A. Review Items:

Form I's, Form V's, and raw data.

B. Evaluation Procedure:

1. Review Form V's and verify that results fall within the specified limits.

2. Check raw data and recalculate the reported recoveries to verify that the results were correctly reported on Form V's. When calculating recoveries, consider results less than the quantitation/reporting limit to be zero.

3. Verify that the field blank was not used for spike analysis.

4. Verify that a matrix spike was prepared at the proper frequency.

5. Verify that samples of the same matrix which have matrix spike recoveries out of criteria are flagged "N" on the Form V and on all applicable sample Form I's.

C. Criteria:

1. A matrix spike analysis must be performed on each group of 20 or fewer samples of a similar matrix for each SDG.

2. Samples identified as field blanks should not be used for spike sample analysis.

3. Spike recoveries must be within the limits of 75-125% or all the associated Form I's and V's must be flagged with an "N" (spike recovery

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limits do not apply when sample concentration exceeds the spike concentration by a factor of four or more).

D. Actions:

1. If a matrix spike analysis was not performed at the proper frequency, a noncorrectable deficiency should be written in the quality assurance review.

2. If a field blank was used for spike analysis, a noncorrectable deficiency should be written in the quality assurance review.

3. If the results or recoveries are misreported on the Form V's, a correctable deficiency should be written in the quality assurance review.

4. If the spike recovery falls outside the recovery limits for an analyte and the Form I's or Form V's have not been flagged "N," a correctable deficiency should be written in the quality assurance review.

5. If the spike recovery is 75-125% and the reported sample results are <IDL, the data is acceptable for use.

6. If the spike recovery is >125% or <75% and the reported sample levels are >IDL, qualify the data for these samples as estimated ("J"). Region II specifies that if the recovery is >200% for solid samples and >150% for aqueous samples, then all positive results should be flagged "R."

7. If the spike recovery falls within the range of 30-74% and the sample results are >IDL, qualify the data for these samples as estimated ("UJ"; "UL" for [illegible]).

8. If the spike recovery results are <30% and the sample results are <IDL, qualify the data for these samples as unusable ("R"). Region II stipulates rejection ("R") at <10%; however, Environmental Standards' criterion is <30%.

9. Per Region II, if a field blank was used for the matrix spike analysis, all associated positive results <4× the spike added should be flagged "J" except in the case when the field blank is the only aqueous sample in the SDG.

10. No actions are taken based solely on the post-digestion matrix spike recoveries. However, these may be used in conjunction with the laboratory

duplicate analyses and the pre-digestion matrix spike recoveries to indicate the possible reason for the poor pre-digestion matrix spike recoveries (sample inhomogeneity, digestion/distillations loss, analytical bias, or sample-specific matrix effects).

11. If examination of the raw data revealed negative concentrations (>2× IDL), flag the "not detected" results "UJ" or "UL" (Region III). If the negative concentration is > 5× the IDL, flag the "not detected" result "R".

VIII. Sample Result Verification:

A. Review Items:

Form I's, Form Xs, Form XIs, Form IXs, Form XIII, raw data, and digestion logs.

B. Evaluation Procedure:

The raw data should be examined to verify the correct calculation of all sample results reported by the laboratory. Digestion logs, instrument printouts, strip charts, etc., should be compared to the reported results on the Form I's and the data tables. This includes the raw data for the determination of percent solids for non-aqueous sediment samples.

1. Examine the raw data for any anomalies (i.e., baseline shifts, negative absorbencies, omissions, legibility, etc.).

2. Verify that there are no transcription or reduction errors (e.g. dilutions, percent solids, sample weights). Also verify that all "not-detected" results are flagged "U" (with the correct quantitation/reporting limit) on all quality control forms used to report the sample results.

3. Verify that results fall within the calibrated range of the instrument used for analysis.

4. Verify that the IDLs have been determined within the current quarter of the sample analysis (or MDLs have been determined within the past year) and that the laboratory is reporting the correct IDLs for the samples.

5. Verify that the laboratory-reported IDLs are ≤ the detection limits required for the project.

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6. Use the Form XIVs to ascertain from which run sequence the laboratory is reporting the results. The particular run that represents the analysis being reported should have an "X" in the box.

C. Criteria:

1. Analyte quantitation for aqueous samples are direct readouts except for microwave digestion, where there is a correction factor of 1.11. Multiply the instrument level by this factor.

2. Analyte quantitation for solid samples are calculated in accordance with the following:

$$\text{Concentration (mg/Kg)} = \frac{(C)(V)}{(W)(S)}$$

where:

C = concentration (mg/L)
V = final volume in mL after sample prep
W = weight of wet sample in g
S = % solids/100

3. IDLs must be determined quarterly on the instruments being used for analysis, and MDLs should be determined annually (NYSDEC specifies that IDLs be determined semi-annually).

4. All reported results must fall within the calibrated range of the instruments used for analysis.

5. The reported IDLs must be less than or equal to the detection limits required for the project.

D. Actions:

1. If the results for any analyte have been misreported on the Form I's, a correctable deficiency should be written in the quality assurance review. Any changes in results should be well documented in the support documentation section and changed on the data tables. (Note in the report that the data tables have been modified.)

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2. If there are any discrepancies found, the laboratory may be contacted to obtain additional information that could resolve differences.

3. If the IDL or MDL studies are not updated within the proper frequency, a noncorrectable deficiency should be included in the quality assurance review.

4. If the IDLs are greater than the detection limits required for the project for mercury, a noncorrectable deficiency should be written into the quality assurance review.

5. If the laboratory has not specified the correct run reported on the Form XIV, a correctable deficiency should be written in the quality assurance review

IX. Field Duplicates

A. Review Items:

Form I's and raw data.

B. Objective:

Field duplicate samples may be obtained and analyzed as an indication of overall precision and sample representativeness. These analyses measure both field and laboratory precision; therefore, the results may have more variability than laboratory duplicates, which measure only laboratory performance. Soil sample duplicate results are expected to have a greater variance than water matrices due to difficulties associated with collecting identical field samples. The reviewer should check with the project manager as to the identity of any blind field duplicates.

C. Evaluation Procedure:

Samples which are field duplicates should be identified. The reviewer should compare the results reported for each sample and duplicate and calculate the relative percent difference (RPD). This tabulation can either be in the narrative section of the report or in the support documentation.

D. Actions:

1. Per Region V, positive results for a target compound should be flagged "J" in the sample and its field duplicate if the following criteria are not met:

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a. A control limit of ± 40% (70% for solids) for the RPD shall be used for sample values greater than 5× the quantitation/reporting limit.

b. A control limit of ±2× the quantitation/reporting limit (±4× the quantitation/reporting limit for solids) shall be used for sample values less than or the quantitation/reporting limit.

2. Per Region I, positive results for a target compound should be flagged "J" in the sample and its field duplicate if the following criteria are not met:

a. A control limit of ± 30% (50% for solids) for the RPD shall be used for sample values greater than 5× the quantitation limit/reporting limit.

b. A control limit of ± the quantitation limit/reporting limit (± 4× the quantitation limit/reporting limit for solids) shall be used for sample values less than 5× the quantitation limit/reporting limit.

c. Per Region II, if the RPD is >60% (when sample and duplicate are ≥ 5× quantitation limit/reporting limit) or if the difference between the sample and field duplicate is > quantitation limit/reporting limit (when sample and/or duplicate are <5× quantitation limit/reporting limit), flag all positive results "J" for aqueous samples.

d. Per Region II, if the RPD is >100% (when sample and duplicate are ≥ 5× quantitation limit/reporting limit) or the difference between the sample and duplicate is >2× quantitation limit/reporting limit (when sample and/or duplicate are <5× quantitation limit/reporting limit), flag all positive results "J" for solid samples.

e. Per Region II, if any value for a sample duplicate pair is < quantitation limit/reporting limit and the other is ≥ 10× quantitation limit/reporting limit, all positive results should be flagged "J."

The above Region-specific criteria are mentioned for completeness and discussion; however, the following criteria will be used in <u>all</u> circumstances:

f. If the RPD is >20% for aqueous samples or 40% for solid samples (when sample <u>and</u> duplicate are ≥ 5× quantitation limit/reporting limit), flag all associated positive results "J."

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g. If the control limit of ± quantitation limit/reporting limit (2× quantitation limit/reporting limit for soils) for results <5× quantitation limit/reporting limit (either sample or duplicate) is exceeded, flag all associated positive results "J." If a result is less than the IDL, use the IDL for comparison purposes. If one result has been flagged "B" or "U" due to blank contamination, use the original reported concentration as real for comparison purposes. If both results are flagged "U" or "B," or if one result is less than the IDL and the other is flagged "B" or "U," comparison is not necessary.

h. Where a triplicate analysis exists, apply an RSD of 20% for aqueous samples and an RSD of 50% for solids for results >5× quantitation limit/reporting limit; use a ± quantitation limit/reporting limit criterion for aqueous sample results and a ±2× quantitation limit/reporting limit criterion for solid sample results if any one of the triplicate set has a concentration less than 5× quantitation limit/reporting limit.

X. Dissolved/Total Mercury Comparison

A. Review Items:

Form I's, raw sample data, and digestion logs.

B. Objective:

To compare the results between dissolved and total analytes.

C. Evaluation Procedure:

Calculate the differences between dissolved and total analytes as a percentage of the total analyte **when the dissolved concentration is greater than the total concentration**. Document comparisons in the narrative section of the report. Note whether the filtered samples were digested.

D. Actions:

Region I protocol and the Functional Guidelines provide no guidance for qualifying data between dissolved and total analyte results.

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Per Region II, if the concentration of any dissolved analyte is >110% of its total concentration, flag all positive results "J." If the concentration of any dissolved analyte is >150% of its total concentration, flag both results "R." No qualification is necessary when the total and dissolved results are < the quantitation/reporting limit.

Environmental Standards, Inc. Policy: If one or both of the results (total and filtered concentrations) are less than 10×IDL use the following criteria:

1. If the difference between the results is greater than the IDL, flag both results as estimated ("J").

2. If the difference between the results is greater than 5×IDL, flag both results as unreliable ("R").

If both results are greater than 10×IDL, then calculate the percent difference using the following equation:

$$\%D = \frac{\text{Total concentration} - \text{Filtered concentration}}{\text{Total concentration}}$$

Apply the following criteria:

3. If the percent difference is greater than 10%, flag both results as estimated ("J").

4. If the percent difference is greater than 50%, flag both results as unreliable ("R").

XI. Overall Assessment of Data

A. Review:

Entire data package, data review results and, if available, Quality Assurance Project Plan, Sampling and Analysis Plan and discussion with the Project Manager.

B. Objective:

The overall assessment of a data package is a quality assurance review in which the data reviewer points out contractual differences, comments, and data qualification with respect to the usability of the data.

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C. Evaluation Procedure:

1. Evaluate any technical problems which have not been previously addressed.

2. If appropriate information is available, the reviewer may assess the usability of the data to assist the data user in avoiding inappropriate use of the data. Review all available information, including the Quality Assurance Project Plan, Sampling and Analysis Plan, and communication with the data user that concerns the intended use and desired quality of these data, keeping in mind the additive nature of analytical problems.

3. Be sure to carefully read the laboratory case narratives and review the Chain-of-Custody.

D. Actions:

1. Use professional judgment to determine if there is any need to qualify data which were not qualified based on the QC previously discussed.

2. Write a quality assurance review to give the user an indication of the analytical limitations of the data. If sufficient information on the intended use and required quality of the data is available, the reviewer should include his/her assessment of the usability of the data within the given context. Include a summary of the important items found during the review of the data in the cover letter, especially those items which may have slowed down or prevented a complete validation of the data package.

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XII. AUTHORITY

This data validation SOP for the analysis of mercury in solid and aqueous samples has been prepared by Environmental Standards, Inc. This SOP represents internal control copy number __ issued to _____ and is not to be photocopied or used by any other entity except Environmental Standards, Inc. without expressed written permission.

SOP approved by:

_____ Date _____

Rock J. Vitale
Quality Assurance Specialist/Principal

Controlled Copy Number: _____
Received by: _____

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STANDARD OPERATING PROCEDURES FOR DATA VALIDATION OF INORGANICS ANALYSIS BY ICP (METHOD 6010A)*

I. INTRODUCTION

This standard operating procedure (SOP) details the procedure for the validation of data from the inductively coupled plasma (ICP) analysis performed by SW-846 Method 6010A. Before samples can be analyzed, the metals must be converted to free elements in solution. (Aqueous samples analyzed for dissolved metals may not necessarily be digested prior to analysis, depending on the laboratory.) This is usually accomplished using the following steps:

Aqueous samples: 100 ml sample is heated with acid, filtered, and adjusted back to 100 ml. (Methods 3005A or 3010A)

Solid samples: 1 to 2 gm of sample (wet weight) is heated with acid, filtered, and adjusted to 100 ml volume. (Method 3050A)

Samples, once solubilized or digested, are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific, atomic-line emission spectra are produced by a radio-frequency ICP. The spectra are dispersed by a grating spectrometer, and the intensities of the lines are monitored by photomultiplier tubes.

SW-846 methods are subject to differing interpretations from the laboratories. In addition, the project-specific quality assurance project plan (QAPP) might include requirements which differ from those presented in the SOP. Therefore, some of the sections in the SOP might not be applicable to all situations.

II. TECHNICAL HOLDING TIMES

A. Review Items

Form I's, Chain-of-Custody records, digestion logs, and Case Narrative

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* **See Section XIII for Authority and Application of this SOP.**

B. Objective

The objective is to ascertain the validity of results based on the holding time of the sample from the time of sample collection to the time of sample analysis.

C. Criteria

The technical holding time criteria for water and solid samples from date of sample collection are as follows:

	Aqueous	Solid
Metals	6 months; preserved to pH <2	6 months

D. Evaluation Procedure

Technical holding times are established by comparing the sampling dates on the Chain of Custody forms with the dates of analysis on the Form I's and the raw data. Examine the sample records to determine if samples were preserved.

E. Action

If technical holding times or preservation criteria are exceeded, document this in the quality assurance (QA) review and qualify the sample results according to the following criteria:

1. If holding times and preservation criteria are not met, all positive results should be qualified "J", estimated, and all "not-detected" results should be qualified "UJ".

2. If holding times are grossly exceeded (if samples are analyzed more than one year from the date of sample collection), the reviewer may use professional judgment and qualify results < instrument detection limit (IDL) as unusable ("R").

3. If the pH of aqueous samples for total metals analysis is greater than 2, and the laboratory did not adjust the pH of the sample (and allow the sample to sit for 24 to 28 hours before digestion), then positive results reported for the affected samples should be qualified as estimated ("J") and "not-detected" results in the affected samples should be flagged "UJ". It should be noted that aqueous samples for dissolved metals analysis are often not

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preserved in the field; these samples are filtered upon receipt at the laboratory and then acid is added until the pH is less than 2.

III. CALIBRATION

A. Review Items

Form IIs and raw calibration data.

B. Objective

Compliance requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable quantitative data. (It should be noted that many laboratories use US EPA Contract Laboratory Program (CLP) specifications instead, where only one standard, within the instrument's linear range, is used for calibration. Initial calibration demonstrates that the instrument is capable of acceptable performance at the beginning of the analysis run, and continuing calibration verification documents that the initial calibration is still valid.

C. Criteria

1. Initial Calibration

Instruments should be calibrated daily and each time the instrument is set up. A blank and three standards should be used in establishing the analytical curve. (It should be noted that many laboratories use the US EPA Contract Laboratory program specifications instead, where only one standard, within the instrument's linear range, is used for calibration.) After instrument calibration, the laboratory should reanalyze the high concentration standard and verify that all results are within 5% of the true value.

2. Continuing Calibration Verification (CCV)

a. Analysis of the CCV result must fall within the control limits of 90-110% recovery (%R) of the true value for all analytes. If the results do not, the analysis must be terminated; the instrument must be recalibrated, the calibration must be revivified, and all samples associated with the unacceptable calibration check must be reanalyzed.

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b. A CCV must be analyzed every 10 samples. The CCV must also be analyzed at the end of the analytical sequence.

c. The CCV must contain all analytes of interest at concentrations at or near the mid-point of the calibration curve and should be prepared from a source independent of the instrument calibration standards.

D. Evaluation Procedure

1. Verify that the instrument was calibrated daily and each time the instrument was set up using the correct number of standards and a blank.

2. Verify that the high calibration standard was analyzed before sample analysis and that all measured concentrations are within 5% of the true concentrations for all analytes.

3. Verify that all instrument calibration verification (ICV) and CCV recoveries fall within the required windows.

4. Check the raw data to verify that the calibration standard values were transcribed correctly on to the Form IIs. Recalculate one or more of the ICV and CCV %R and verify that the recalculated value agrees with the laboratory-reported values on the Form IIs.

5. Verify that a CCV was analyzed every 10 samples and at the end of the analytical run.

E. Actions

1. If the appropriate number of standards were not used for initial calibration, or if the instrument was not calibrated daily and each time the instrument was set up, consult with a Senior Chemist and the Project Manager about the possible effect on data quality. If it is deemed necessary, qualify the data as unusable ("R").

2. If the ICV or CCV %R falls outside the acceptance windows, use professional judgment to qualify all associated data. The following qualifications will be applicable to the samples preceding and the samples following the CCV out of criterion. If the ICV is out of the criterion, the

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entire sequence will be qualified. The following guidelines are recommended:

a. If the ICV or CCV %R falls outside the acceptance windows but within the ranges of 75-89% or 111-125%, qualify results >IDL as estimated ("J").

b. If the ICV or CCV %R is within the range of 111-125%, results <IDL are acceptable.

c. If the ICV or CCV %R is 75-89%, qualify results <IDL as estimated ("UJ").

d. If the ICV or CCV %R is <75%, qualify all positive and "not-detected" results as unusable ("R").

e. If the ICV or CCV %R is >125%, qualify results >IDL as unusable ("R"); results <IDL are acceptable.

IV. BLANKS

A. Review Items

Form IIIs, Form I's, and raw data

B. Objective

The assessment of method, field, or equipment blank analysis results is to determine the existence and magnitude of contamination problems. The criteria for the evaluation of blanks apply to any blank associated with the samples. If problems with any blank exist, all associated data must be carefully evaluated to determine whether or not there is an inherent variability in the data, or if the problem is an isolated occurrence not affecting other data.

C. Criteria

1. No contaminants should be found in the blank at levels greater than three standard deviations of the background mean.

2. An initial calibration blank must be analyzed immediately following the ICV. A continuing calibration blank (CCB) must be analyzed after every

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10 samples (following the CCV). The CCB must also be analyzed at the end of the analytical sequence. Refer to the project-specific QAPP for frequency at collecting field or equipment blanks.

D. Evaluation Procedure

1. Review the results reported on the Form III, as well as the raw data for all blanks, and verify that the results were accurately reported.

2. Verify that the calibration blanks were analyzed at the proper frequency.

3. Verify that the field or equipment blanks were collected at the proper frequency.

E. Action

1. Action in the case of unsuitable blank results depends on the circumstances and origin of the blank. Any blank with a value below the negative IDL or method detection limit (MDL) must be carefully evaluated to determine its effect on the sample data.

2. In instances where more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration of a contaminant. The results of ICBs and CCBs are applied to samples analyzed on the same instrument during the same analytical run (beginning with the initial calibration) as the CCB. Field and equipment blanks are associated with samples collected on the same day as the field or equipment blank (unless only one was collected over several day period; then the field or equipment blank results are applicable all samples collected during that period). The sample result must not be corrected by subtracting any blank value. Action levels should be calculated that are five times the maximum concentration of each contaminant detected in any blank. No positive results should be reported unless the concentration of the analyte in the sample exceeds five times the amount detected in any blank.

NOTE: The reviewer should note that the blank analyses may not involve the same weights, volumes, or dilution factors as the associated samples. In particular, solid sample results reported on the Form I's will not be on the same bases (e.g., units, dilutions) as the calibration blank data reported on

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the Form IIIs. Sample weights, volumes, and dilution factors must be taken into consideration when applying the 5× criteria.

Sample results should be reported as follows:

a. If an analyte is detected in the blank but not in the sample, no action is taken.

b. Positive results less than the action level (5× the associated blank concentration) shall be reported with a "U".

c. Positive results greater than the action level shall be reported unqualified.

V. ICP INTERFERENCE CHECK SAMPLE ANALYSIS

A. Review Items

Form IVs and raw data.

B. Objective

The ICP interference check sample (ICS) analysis is performed to verify the laboratory's interelement and background correction factors. Most laboratories will analyze two solutions as part of the ICS - solution A, containing high levels of only the common interferents iron, magnesium, calcium, and aluminum and solution AB, which contains high levels of the interferents and low concentrations of the other target elements.

C. Criteria

1. An ICS analysis must be run at the beginning and end of each sample analysis run, or a minimum of twice per 8-hour working shift, whichever is more frequent.

2. Results for the ICS solution AB (ICSAB) analysis should fall within the control limits of ± 20% of the true value.

3. If the laboratory is using a Trace ICP (or another such ICP that is capable of reporting very low concentrations of the toxic metals), then the

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concentrations reported for the toxic metals (all metals with reporting limits less than 10µg/l) shall be within ±2×RL.

D. Evaluation Procedure

1. Verify that the ICS was analyzed at the proper frequency.

2. Verify that the %R for the ICSAB is 80-120%.

3. Recalculate from the raw data one or more recoveries and verify that their calculated value agrees with the laboratory reported values on the Form IV.

4. Check ICS raw data for results with an absolute value >IDL for those analytes which are not present in the ICSA solution (if analyzed). Results greater than twice the absolute value of the IDL indicate either a positive or negative interference and must be qualified (whether or not the element is a toxic metal).

E. Action

1. If the ICS was not analyzed at the proper frequency, the data may be affected. Use professional judgment to qualify the data.

2. For samples with concentrations of Al, Ca, Fe, and Mg which are comparable to or greater than their respective levels in the ICS:

   a. If the ICSAB recovery for an element is >120% and the reported sample results are <IDL, this data is acceptable for use.

   b. If the ICSAB recovery for an element is >120% and the reported sample results are >IDL, qualify the affected data as estimated ("J").

   c. If the ICSAB recovery for an element falls between 50% and 79% and reportable quantities of the analyte were detected, qualify the affected data as estimated ("J").

   d. If an analyte is not detected in the sample, and the ICSAB recovery for the analyte falls within the range of 50-79%, the possibility of

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false negatives may exist. Qualify the data for these samples as estimated ("UJ").

e. If the ICSAB recovery results for an element are <50%, qualify the affected data as unusable ("R").

3. For positive analyses (non-ICSA constituents) in the ICSA (not reported as being truly in the ICSA) that are greater than 2× IDL, qualify as estimated ("J") positive results up to 5× the concentration level observed in the ICSA in the sample displaying the high interferent levels for those samples that have >50% of any of the ICSA interferents. "Not-detected" results are not qualified due to this issue.

4. If non-ICSA analytes are reported as being "true" values in the ICSA, a comment must be included in the QA review stating that it is ambiguous whether the presence of such analytes reported as "true" values represents a contractual noncompliance.

5. For negative interferences that are greater than the absolute value of 2× IDL, applicable positive sample results (up to 5× the level of the analyte observed in the ICSA) should be flagged "J", and "not-detected" results should be flagged "UJ". Note: Apply only when the interferent is >50% of the ICSA in samples.

6. In general, the sample data can be accepted if the concentration of Al, Ca, Fe, and Mg in the sample are found to be less than or equal to their respective concentrations in the ICS. If other elements are present in the samples at >10 mg/l, the reviewer should investigate the possibility of other interference effects in accordance with the analytical protocol. These analyte concentration equivalents presented in the protocol should be considered only as estimated values, since the exact value of any analytical system is instrument-specific. Therefore, estimate the concentration produced by an interfering element. If the estimate is >2× contract-required detection limit (CRDL) and also greater than 10% of the reported concentration of the affected element, qualify the affected result as estimated ("J").

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VI. LABORATORY CONTROL SAMPLE ANALYSIS (LCS)

A. Review Items

Form VII and raw data

B. Objective

The LCS analysis is designed to serve as a monitor of the efficiency of the digestion procedure.

C. Criteria

1. Method 6010A refers to a quality control (QC) sample but gives no frequency or limits. Refer to the project-specific QAPP for frequency, recovery criteria, and corrective actions for LCS analyses. If the laboratory includes a QC sample (LCS), and the QAPP does not give guidance for the LCS, professional judgment should be used as listed below.

   a. An LCS should be analyzed for each analyte using the same sample preparations and methods employed for the samples received. One LCS should be prepared and analyzed per matrix and per digestion batch per sample delivery group (SDG).

   b. All aqueous LCS results should fall within the control limits of 80-120%. Antimony and silver may be excluded from this criterion.

   c. All solid LCS results must fall within the control limits established by the US EPA and provided by the US EPA with the solid LCS.

2. Action

   a. Aqueous LCS:

      i) If the LCS recovery for any analyte falls within the range of 50-79% or 120-150%, qualify results >IDL as estimated ("J"). However, positive results for analytes displaying recoveries >150% should be flagged "R".

      ii) If results are <IDL and the LCS recovery is greater than 120%, the data are acceptable.

iii) If results are <IDL and the LCS recovery falls within the range of 50-79%, qualify the data for these samples as estimated ("UJ" or "UL").

iv) If LCS recovery results are <50%, qualify the data for these samples as unusable ("R").

b. Solid LCS

For solid LCSs, recoveries outside the 70-130% range shall require qualification. Positive results are flagged "J"; "not detected" results associated with solid LCS recoveries <70% are flagged "UJ". The only exception is when the true value (the certified concentration of the analyte in the LCS) is below 3× the IDL or the CRDL (whichever is lower), in which case no qualification is warranted from a recovery perspective.

VII. DUPLICATE SAMPLE ANALYSIS

A. Review Items

Form VIs and raw data

B. Objective

Duplicate analyses are indicators of the precision of the sample results. Laboratory duplicate samples measure the laboratory's precision in the sample digestion and analysis.

C. Criteria

1. Samples identified as field blanks should not be used for duplicate sample analysis.

2. A control limit of 20% for aqueous samples (40% for solid samples) for the relative percent difference (RPD) shall be used for sample values >5 times the IDL. A control limit of ±IDL for aqueous samples (±2×IDL for solid samples) shall be used when the sample results are <5×IDL.

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3. A duplicate sample must be prepared and analyzed for every analytical batch digested or with every 20 samples, whichever is more frequent. (Refer to the QAPP for project-specific guidelines.)

D. Evaluation Procedure

1. Review Form VI and verify that results fall within the control limits.

2. Check the raw data and recalculate one or more RPD to verify that results have been correctly reported on the Form VI.

3. Verify that the field blank was not used for duplicate analysis.

4. Verify that duplicates were prepared at the required frequency.

5. The RPD between replicate determinations is to be calculated as follows:

where:

RPD = relative percent difference
D1 = first sample value
D2 = second sample value (replicate)

E. Action

1. If duplicate analysis results for a particular analyte fell outside the appropriate control windows, qualify the positive results for that analyte in all samples of the same matrix as estimated ("J"). "Not-detected" results are not necessarily qualified due to duplicate analysis results.

2. If the field blank was used for duplicate analysis, all other QC data must be carefully checked and professional judgment exercised when evaluating data.

VIII. MATRIX SPIKE/MATRIX SPIKE DUPLICATES

A. Review Items

Form V's and raw data

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B. Objective

The matrix spike/matrix spike duplicate sample analysis is designed to provide information about the effect of the sample matrix on the digestion and measurement methodology. It should be noted that many laboratories will analyze an MS and laboratory duplicate rather than an matrix spike/matrix spike duplicate. Refer to the QAPP for project-specific details.

C. Criteria

1. Matrix spike analyses are required every 20 samples or with every batch of sample prepared, whichever is more frequent.

2. Samples identified as field blanks cannot be used for spike sample analysis.

3. Spike recovery (%R) must be within the limits of 75-125% for ICP analysis. However, spike recovery limits do not apply when sample concentration exceeds the spike concentration by a factor of 4 or more.

4. If the matrix spike recovery does not meet criteria, a post-digestion spike is recommended and reported for ICP analyses.

5. The RPD for the matrix spike/matrix spike duplicate recoveries should be less than or equal to 20% for aqueous samples and 40% for solid samples.

D. Evaluation Procedure

1. Review Form V's and verify that results fall within the specified limits.

2. Check raw data and recalculate one or more %R and RPDs to verify that the results were correctly reported on the Form V's.

3. Verify that the field blank was not used for spike analysis.

4. Verify that a matrix spike was prepared at the proper frequency (5% or per analytical batch, whichever is more frequent or per the QAPP).

E. Action

1. If the spike recovery if >125% for ICP and the reported sample results are <IDL, the data is acceptable for use.

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2. If the spike recovery if >125% or <75% for ICP and the reported samples levels are >IDL, qualify the data for these samples as estimated ("J").

3. If the spike recovery falls within the range of 30-74% for ICP and the sample results are <IDL, qualify the data for these samples as estimated ("UJ").

4. If the spike recovery results fall <30% and the sample results are <IDL, qualify the data for these samples as unusable ("R").

5. If the field blank was used for matrix spike analysis, all other QC data must be carefully checked and professional judgment exercised when evaluating the data.

6. If the RPD between the two series for a particular element exceeds 20% for aqueous samples (40% for solid samples), qualify positive results for that element in all associated samples as estimated ("J"). "Not-detected" results are not qualified based on this issue.

IX. ICP SERIAL DILUTION ANALYSIS

A. Review Items

Form IXs and raw data

B. Objective

Serial dilution analysis determines whether significant physical or chemical interferences exist due to sample matrix.

C. Criteria

1. If the analyte concentration is sufficiently high (concentration in the original sample is minimally a factor of 10 above the IDL), the laboratory should report the results of a five-fold dilution. Results that do not agree within 10% of the original results may be flagged with "E" by the laboratory.

2. A serial dilution is recommended for each matrix analyzed. Refer to the QAPP for project-specific requirements.

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D. Evaluation Procedure

1. Verify that reported results for the serial dilution meet required criteria of ±10%D for elements with positive results in the initial sample analysis greater than 10 × ±IDL.

2. Check the raw data and recalculate the %D to verify that the dilution analysis results agree with initial sample results reported on the Form IXs.

3. Check the raw data for evidence of negative interference (i.e., results of the undiluted samples are significantly higher than the original sample).

E. Action

1. When specified criteria are not met (>10%D when the initial sample result was greater than 10× IDL), qualify the associated data as estimated ("J").

2. If evidence of negative interference is found, use professional judgment to qualify the data. Not-detected results are not generally qualified due to high %Ds in the serial dilution analysis.

X. SAMPLE RESULT VERIFICATION

A. Review Items

Form I's, digestion logs, and raw data

B. Objective

To ensure that the reported quantitation results are accurate.

C. Criteria

Analyte quantitation must be calculated in accordance with Method 6010A.

D. Evaluation Procedure

The raw data should be examined to verify the correct calculation of sample results reported by the laboratory. Digestion logs, instrument printouts, strip charts, etc., should be compared to the reported results on the Form I's.

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1. Examine the raw data for any anomalies (e.g., baseline shifts, negative absorbance, omissions, legibility, etc.).

2. Verify that there are no transcription or reduction errors (e.g., dilutions, percent solids, sample weights).

3. Verify that results fall within the linear range of the ICP and within the calibrated range for the non-CLP parameters.

4. Verify that sample results are >5x the IDL, if ICP analysis results are used for arsenic, thallium, selenium, or lead, unless the laboratory used an ICP capable of very low detection limits (<10 µg/L for arsenic and thallium, <5µg/L for selenium, and <3ug/L for lead) for these elements.

E. Action

If there are any discrepancies found, the laboratory may be contacted to obtain additional information that could resolve differences. If a discrepancy remains unresolved, the reviewer may determine if qualification of the data is warranted. If the laboratory reported results from an ICP for an element with an IDL greater than the CLP CRDL and the result does not exceed five times the reported IDL, flag the positive result as estimated ("J").

XI. FIELD DUPLICATES

A. Review Items

Form I's and raw data

B. Objectives

Field duplicate samples may be taken and analyzed as an indication of overall precision. These analyses measure both field and laboratory precision; therefore, the results may have more variability than laboratory duplicates which measure only laboratory performance. It is also expected that soil duplicate results will have a greater variance than water matrices due to difficulties associated with collecting identical field samples.

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C. Criteria

There are no specific review criteria for field duplicate analyses comparability. Refer to the QAPP for project-specific frequency and precision criteria.

D. Evaluation Procedure

Samples which are field duplicates should be identified. The reviewer should compare the results reported for each sample and duplicate and calculate the RPD.

E. Action

Positive results for a target compound should be flagged "J" in the sample and its duplicate if the following criteria are not met:

1. A control limit of 20% (40% for solids) for the RPD shall be used for sample values greater than 5× the CRDL.

2. A control limit of the CRDL (±2× the CRDL for solids) shall be used for samples with at least one value less than 5× the CRDL.

XII. OVERALL ASSESSMENT OF DATA

A. Review Items

Entire data package, data review results, and if available, QAPP, and the Sampling and Analysis Plan.

B. Objective

The overall assessment of a data package is a brief narrative in which the data reviewer expresses concerns and comments on the quality and, if possible, the usability of the data.

C. Criteria

Assess the overall quality of the data.

Review all available materials to assess the overall quality of the data, keeping in mind the additive nature of analytical problems.

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D. Evaluation Procedure

1. Evaluate any technical problems which have not been previously addressed.

2. If appropriate information is available, the reviewer may assess the usability of the data to assist the data user in avoiding inappropriate use of the data. Review all available information, including the QAPP, the Sampling and Analysis Plan, and communication with the data user that concerns the intended use and desired quality of these data.

E. Action

1. Use professional judgment to determine if there is any need to qualify data which were not qualified based on the QC previously discussed.

2. Write a brief narrative to give the user an indication of the analytical limitations of the data. If sufficient information on the intended use and required quality of the data are available, the reviewer should include his/her assessment of the usability of the data within the given context.

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XIII. AUTHORITY

This data validation SOP for the analysis for halogenated and aromatic volatile organic compounds has been prepared by Environmental Standards, Inc. This SOP represents internal control copy _____ issued to _____ and is not to be photocopied or used by any other entity except Environmental Standards, Inc. without expressed written permission.

SOP approved by:

_____ Date: _____

Rock J. Vitale, CPC
Technical Director of Chemistry/Principal

Control Copy No.: _____

Received by: _____

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STANDARD OPERATING PROCEDURES FOR DATA VALIDATION

OF CHLORINATED HERBICIDES BY GC/ECD (METHOD 8150/8151)*

I. METHOD SUMMARY

This method is for the analysis of chlorinated herbicides in aqueous samples. Samples are spiked with a surrogate compound (typically 2,4-DB or 2,4-DCAA) and extracted with diethyl ether. The extract is esterified (Method 8150) or derivatized (Method 8151) prior to sample analysis. The extract is dried, and concentrated and subsequently analyzed by gas chromatography (GC). The compounds of interest are detected through the use of an electron capture detector (ECD).

II. TECHNICAL HOLDING TIMES

A. Review Items

Analytical result pages, Chain-of-Custody Records, raw data, and Case Narrative.

B. Objective

The objective is to ascertain the validity of results based on the holding time of the sample from the time of collection to the time of analysis.

C. Criteria

Technical requirements for sample holding times are based on the project-specific QAPP. The holding time criteria for chlorinated herbicides in cooled (4°±2°C) water samples is 7 days from sample collection to extraction and 40 days from sample extraction to analysis. The recommended holding times for solid samples is 14 days from sample collection to extraction and 40 days from sample extraction to analysis.

D. Evaluation

Technical holding times are established by comparing the sampling dates on the Chain-of-Custody forms with the dates of analysis on the analytical result pages and the raw data. Examine the sample records to determine if samples were preserved [cooled (4°±2°C)].

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* **See Section XII for authority and application of this SOP.**

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E. Action

If technical holding times are exceeded, document in the quality assurance review that holding times were exceeded and qualify the sample results according to the following criteria:

1. If extraction of aqueous samples was performed more than 7 days and less than 14 days from the date of sample collection, flag positive results as estimated (flagged "J") and "not-detects" as "UJ".

2. If extraction of aqueous samples was performed more than 14 days from the date of collection, flag positive results as estimated (flagged "J") and "not-detects" as "R".

3. If the extracts for the aqueous samples were analyzed more than 40 days but less than 80 days from the date of sample extraction, flag positive results as estimated (flagged "J") and "not-detects" as "UJ".

4. If the extracts for the aqueous samples were analyzed more than 80 days from the date of sample extraction, flag positive results as estimated (flagged "J") and "not-detects" as "R".

5. If extraction of solid samples was performed more than 14 days and less than 28 days from the date of sample collection, flag positive results as estimated (flagged "J") and "not-detects" as "UJ".

6. If extraction of solid samples was performed more than 28 days from the date of collection, flag positive results as estimated (flagged "J") and "not-detects" as "R".

7. If the extracts for the solid samples were analyzed more than 40 days but less than 80 days from the date of sample extraction, flag positive results as estimated (flagged "J") and "not-detects" as "UJ".

8. If the extracts for the solid samples were analyzed more than 80 days from the date of sample extraction, flag positive results as estimated (flagged "J") and "not-detects" as "R".

9. If samples are received at temperatures greater than 6°C, flag positive results as estimated (flagged "J") and "not-detects" as "UJ".

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III. INITIAL CALIBRATION

A. Review Items

Calibration summary forms, integration reports and chromatograms.

B. Objective

Compliance requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable qualitative and quantitative data for herbicide compounds.

C. Criteria

1. Initial calibration standards containing the chlorinated herbicide target compounds are analyzed at five concentrations (whose range depends on the individual compound) at the beginning of each analytical sequence or as necessary if the ongoing calibration acceptance criteria are not met. The low concentration standard should be at or near the method detection limit. The initial calibration standards will be used to define the working range. It should be noted that the methods allow for either the internal or external standard method for quantitating positive results.

2. The low standard must be visible on the chromatogram.

3. The percent relative standard deviation (%RSD) for the initial calibration standards must be ≤20% for all compounds for linearity to be demonstrated. If the RSD is in excess of 20%, then the calibration curve (binomial, cubic, etc.) must be used for the particular compound.

D. Evaluation

1. Verify that the correct concentrations of standards were used for the initial calibration based on the laboratory analytical SOP.

2. Verify that the correct initial calibration was used for all samples.

3. Verify if all sample results were calculated using the initial calibration in the proper way. Specifically, if the RSD for a particular compound is ≤20%, the

average response factor should be used. If the RSD for a particular compound is >20%, the entire curve representing the working standards must be used.

4. Evaluate the initial calibration RFs for all target compounds.

   a. Check and recalculate the response factors (RFs) and average RFs for three target compounds; verify that the recalculated value(s) agrees with the laboratory-reported value(s).

   b. Verify that the low calibration standard is clearly visible on the chromatogram.

5. Evaluate the %RSD for all target compounds.

   a. Check and recalculate the %RSD for three target compounds; verify that the recalculated value agrees with the laboratory- reported values.

   b. Verify that all target compounds have a %RSD less than or equal to 20.0% if the average response factor is used for quantitation.

E. Action

1. If any target compound result is associated with a low concentration initial calibration standard that is not visible on the chromatogram, professional judgment must be used to determine the magnitude of the bias.

   a. Flag "not-detects" for that compound with an "UJ". If the standards indicate a severe lack in sensitivity (e.g., the higher calibration standards are barely visible), the reviewer may elect to flag "not-detects" for that compound with an "R".

2. If any target compound has a %RSD greater than 20% <u>and</u> the average response factor was used for quantitation:

   a. Flag positive results for that compound as estimated (flagged "J").

   b. "Not-detects" for that compound may be qualified using professional judgment.

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IV. CONTINUING CALIBRATION

A. Review Items

Calibration summary forms, integration reports, and chromatograms.

B. Objective

Continuing calibrations are performed to verify that the initial calibration curve is still acceptable for quantitation of results with respect to sensitivity and accuracy on a day-to-day basis.

C. Criteria

1. Continuing calibration standards containing target compounds and surrogate compounds are analyzed before samples are analyzed and after all samples have been analyzed.

2. The concentration of the continuing calibration check must be at the midpoint of the curve.

3. The percent difference (%D) between the predicted response and the observed response must not differ by more than 15%. If >15% difference is observed, the continuing calibration must be reinjected once. If the criterion is still not met, a new initial calibration must be performed.

4. All succeeding continuing calibrations after the first continuing calibration standard has been used to establish daily retention time windows must be within the established retention time windows.

D. Evaluation

1. Verify that the continuing calibration was run at the required frequency and that the continuing calibration was compared to the correct initial calibration.

2. Evaluate the continuing calibration RF for all target compounds:

   a. Quantitatively verify that the response factors were calculated properly; verify that the recalculated values agree with the laboratory-reported values. (Recalculate three values for each continuing calibration).

b. Verify that the peaks for the continuing calibrations are clearly visible on the chromatograms.

3. Evaluate the %D between the expected response from the initial calibration and the observed response from the continuing calibration for all compounds.

a. Check and recalculate the %D on three target compounds, verify that the recalculated values agree with the laboratory- reported values.

b. Verify that the %D is ≤15% for all target compounds.

4. Verify that after the daily retention time windows have been established that all target analytes in the subsequent calibration checks are within the established retention time windows.

E. Action:

1. If initial or continuing calibrations were not performed at the specified frequency, a statement to this effect should be indicated in the quality assurance review. In addition:

a. Flag positive results for that compound as estimated (flagged "J").

b. Flag "not-detects" for that compound with a "UJ" or, in severe cases, "R".

2. If any target compound has a %D greater than 15% in either the continuing calibration before or after the applicable project samples:

a. Qualify positive results for that compound as estimated (flagged "J") on both sides of the noncompliant standard back to the last compliant calibration.

b. "Not-detects" for that compound may be qualified "UJ" if the bias is in the direction of a sensitivity decrease. If the bias is in the direction of a sensitivity increase, data may be acceptable for "not- detected" sample results.

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3. If any target compound is outside the daily established retention time windows, the associated sample chromatograms must be carefully evaluated using reviewer-generated expanded retention time windows.

   a. If the chromatograms reveal the absence of peaks possibly corresponding to the target compounds of interest using expanded retention time windows, data usability is not affected. A notation should be included in the quality assurance review.

   b. If the chromatograms reveal peaks corresponding to the target compounds of interest using expanded retention time windows, "not-detected" as well as reported positive sample results for the compound outside the retention time window should be flagged "R". This qualification should extend to samples on both sides of the noncompliant standard back to the last compliant calibration.

4. If target analyte peaks in the continuing calibration are not visibly present on the chromatograms, "not-detected" sample results for those analytes should be flagged "R".

V. METHOD AND FIELD/EQUIPMENT BLANKS

A. Review Items

QC summary forms, chromatograms and integration reports.

B. Objective

The assessment of blank analysis results determines the existence and magnitude of contamination problems. The criteria for evaluation of blanks apply to any blank associated with the samples. If problems with any blank exist, all associated data must be carefully evaluated to determine whether or not there is an inherent variability in the data or if the problem is an isolated occurrence not affecting other data. If the laboratory blank has reportable target analytes (at or above the QL), the entire sample batch is reextracted and reanalyzed.

C. Criteria

1. No contaminants should be found in the method blanks.

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2. A method blank analysis must be performed at least once for each extraction batch.

3. The method blank must be analyzed on each GC system used to analyze samples for each type of analysis.

D. Evaluation

1. Review the results of all associated blanks on the forms and raw data (chromatograms and integration reports) to evaluate the presence of target compounds in the blanks.

2. Verify that a method blank analysis has been reported for each extraction batch on each GC system used to analyze samples.

E. Action

If the appropriate blanks were not analyzed with the frequency described in Criteria 2 and 3 in Section V.C, then the reviewer should use professional judgment to determine if the associated sample data should be qualified.

Action in the case of unsuitable blank results depends on the origin and circumstances of the blank.

Positive sample results are not qualified for associated blank contamination unless the concentration of the compound in the sample is less than or equal to 5-times (5×) the amount for target compounds. In instances where more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration of contaminant. The results must not be corrected by subtracting any blank value.

Specific actions are as follows:

1. If a target compound is found in a blank but not found in the sample, no action is taken.

2. If the sample result is greater than the quantitation limit (QL) but less than the required amount (5×) from the blank result, the sample results are qualified as "not-detected" ("U").

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3. If the sample result is positive but less than the QL, and is less than the required amount (5×) from the blank result, the result is raised to the QL and is flagged as "not-detected" ("U").

4. If the sample result is greater than the required amount (5×) from the blank result, the sample results are not-qualified.

5. If gross blank contamination exists (i.e., saturated peaks on the GC), all affected compounds in the associated samples should be qualified as "R" due to interferences. Professional judgment must be exercised in these cases.

VI. SURROGATE RECOVERY

A. Review Items

QC summary forms, integration reports, and chromatograms.

B. Objective

Laboratory performance (accuracy and extraction efficiency) on individual samples and blanks is established by means of spiking activities. All samples are spiked with the surrogate compound (typically 2,4-DB or 2,4-DCAA) prior to sample extraction.

C. Criteria

1. One surrogate compound (typically 2,4-DB or 2,4-DCAA) is added to all samples and blanks prior to extraction and esterification/derivatization to measure their recovery in environmental samples and blank matrices.

2. Recoveries for the surrogate compound are typically specified in the QAPP or by the laboratory. If recoveries are not specified, utilize a criterion of 30-120% for samples. If any recoveries are <30%, applicable samples should be reextracted.

D. Evaluation

1. Check raw data (i.e., chromatograms and integration reports) to verify the recoveries on the surrogate recovery QC summary form. Check for any calculation or transcription errors.

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2. The following should be determined from the surrogate recovery QC summary form(s):

   a. If any surrogate compound is below the acceptance criteria, there should be a reanalysis to confirm that the noncompliance is due to sample matrix effects rather than laboratory deficiencies.

   b. The laboratory failed to perform appropriately if a surrogate recovery was below criteria with no evidence of reextraction and reanalysis. Be certain that the laboratory is using a criterion for reextraction. Note the laboratory's criterion may not necessarily be the 30-120% guidance criterion stipulated in this SOP.

   c. Verify that no blanks have surrogate recoveries outside the criteria.

E. Action:

Data are qualified based on surrogate compound results. If the recovery for the surrogate compound is out of specification, For surrogate compound recoveries out of specification, the following approaches are suggested:

1. If the surrogate recovery is greater than the upper acceptance limit:

   a. Positive target compounds are qualified as estimated (flagged "J").

   b. "Not-detected" results for target compounds should not be qualified.

2. If the surrogate recovery is greater than or equal to 10% but less than the lower acceptance limit:

   a. Positive target compounds are qualified as estimated (flagged "J")

   b. "Not-detected" results for target compounds should be qualified "UJ"

   Note: When there is an unacceptable surrogate compound recovery followed by successful reextraction/reanalysis, the laboratory is required to report only the results for the successful run.

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3. If the surrogate has a recovery less than 10%:

   a. Positive target compound results are qualified as estimated (flagged "J").

   b. "Not-detected" results for target compounds should be qualified "R".

VII. INTERNAL STANDARDS (if used)

A. Review Items

QC summary forms, integration reports, and chromatograms.

B. Objective

Internal standards performance criteria ensures that GC sensitivity and response are stable during each analysis. Internal standards are used for the quantitation of positive results of all compounds and surrogates in the analysis.

C. Criteria

1. Internal standard compounds are added to all field samples, QC samples, and blanks immediately before injection into the GC to ensure that sensitivity and response are stable during each analysis.

2. Criteria for internal standards are typically specified in the QAPP or by the laboratory. If criteria are not specified, utilize the following guidance:

   a. Retention times of the internal standards in the samples and blanks must not vary more than ±30 seconds from the retention times of the associated calibration standard, and are county of the internal standards in the samples and blanks must not vary more than a factor of two (-50% to +100%) from the associated calibration standard for all samples.

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D. Evaluation

1. Verify internal standard compounds were added to all samples and blanks (if the internal standard method of quantitation is used for the analysis).

2. If any internal standard compound is outside the acceptance criteria (laboratory-specified), there should be a reanalysis to confirm that the noncompliance is due to sample matrix effects rather than laboratory deficiencies.

E. Action

Data are qualified if internal standard compound results are out of specification. For internal standard compounds out of specification, the following approaches are suggested:

1. If an internal area county for a sample is greater than the upper acceptance limit, flag positive results "J" and "not-detected" results "UJ" for the compounds quantitated from the internal standard.

2. If an internal standard area count for a sample is less than the lower acceptance limit but greater than or equal to 10% of the associated calibration internal standard, flag positive results "J" and "not-detected" results "UJ" for the compounds quantitated from the internal standard.

3. If an internal standard area count for a sample is less than 10% of the associated calibration internal standard, flag positive results "J" and "not-detected" results "R" for the compounds quantitated from the internal standard.

4. When the internal standard retention time varies by more than 30 seconds and no peaks are observed in the sample chromatogram, then there may be no impact on data usability. However, if peaks are observed in the sample chromatogram, professional judgment will be exercised on a case-by-case basis.

VIII. MATRIX SPIKES/MATRIX SPIKE DUPLICATES, BLANK SPIKES AND LABORATORY CONTROL SAMPLES

A. Review Items

QC summary forms, chromatograms, and integration reports.

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B. Objective

Data for matrix spikes (MSs)/Matrix Spike Duplicates (MSDs) are generated to determine long-term accuracy and precision of the analytical method on various matrices and to demonstrate acceptable compound recovery by the laboratory at the time of sample analysis. These data alone are not used to evaluate the accuracy of other samples. The data for blank spikes (BSs) or laboratory control samples (LCSs) are generated to determine analytical accuracy. The results of blank spikes are used to assess the accuracy of the entire sample batch.

C. Criteria

1. MS/MSD samples are analyzed at a frequency of one per 20 samples. BS (or LCS) samples may also be analyzed at a frequency of one per 20 samples, or one per extraction batch, whichever is more frequent.

2. MS/MSD and BS (or LCS) recoveries and MS/MSD RPDs should be within the following criteria. Note each laboratory on each project (QAPP) may specify different criteria. See the QAPP for project-specific recovery and RPD criteria. The following criteria are presented as guidance.

Compound	%R	RPD
2,4-D	50-135%	20%
2,4,5-TP	50-135%	20%
2,4,5-T	50-135%	20%

3. If any recovery is below the acceptance criteria (laboratory-generated only) in the BS (or LCS) analysis, all associated samples must be reextracted and reanalyzed.

D. Evaluation

1. Verify that an MS/MSD and BS (or LCS) were analyzed at the required frequency.

2. Inspect results for the MS/MSD and BS (or LCS) recoveries and the MS/MSD RPDs on the QC summary forms and verify that the results for the recoveries are within the specified limits.

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3. Verify transcriptions from raw data and verify calculations.

4. Calculate the RSD for the positive results of unspiked compounds in the initial and MS/MSD analyses.

E. Action

1. No action is taken on MS/MSD data alone. However, using informed professional judgment, the data reviewer may use the MS/MSD results in conjunction with the other QC criteria and determine the need for some qualification of the data. Action may be taken on the entire batch based on the BS (or LCS) recoveries.

2. In the instance where it can be determined that the results of the MS/MSD affect only the sample spiked, then the following criteria should be used for the sample that was spiked:

   a. If the recovery of a matrix spike compound in the MS/MSD has a recovery greater than the upper acceptance limit, positive results for that compound in the unspiked sample should be considered estimated (flagged "J").

   b. If the recovery of a matrix spike compound in the MS/MSD has a recovery less than the lower acceptance limit and >10%, the positive result for that compound in the unspiked sample should be considered estimated (flagged "J") or the "not-detected" result should be flagged "UJ".

   c. If the recovery of a matrix spike compound in the MS/MSD has a recovery less than 10%, positive results for that compound in the unspiked sample should be considered estimated (flagged "J") and "not-detected" results should be flagged "R".

   d. If the RPD is outside the acceptance criteria, positive sample results for those analytes should be considered estimated and flagged "J".

3. In instances where the BS (or LCS) recoveries are outside acceptance criteria, Actions 2a, 2b and 2c above are applied to <u>all</u> samples (of similar matrix) in that extraction batch.

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4. If the RSD for the positive results for an unspiked target compound in the initial and MS/MSD analyses exceeds 30%, flag the positive result for the compound in the initial sample analysis as estimated ("J"). Exception: if one or more of the results in the initial and MS/MSD analyses is less than 5×QL, flag the positive result in the initial sample analysis "J" if the three results fall outside a 2×QL window.

IX. COMPOUND QUANTITATION AND REPORTED QUANTITATION LIMITS

A. Review Items

QC summary forms, Case Narrative, integration reports and chromatograms.

B. Objective

The objective is to ensure that reported quantitative results and reported quantitation limits (QLs) are accurate.

C. Criteria

1. Compound quantitation, as well as the adjustment of the QLs, must be calculated according to the correct equation specified in the analytical SOP.

2. The compound quantitation must be based on the average RF from the four initial calibration standards if the RSD is <20%. If the RSD is >20%, the curve must be used for quantitation.

D. Evaluation

1. Verify that the reported quantitation limits are less than or equal to the QAPP-specified QLs. If sample dilution is necessary due to elevated target compound concentrations, or if interference related to the sample matrix is observed, the QLs reported by the laboratory may exceed required limits.

2. For all samples, raw data should be examined to verify the correct calculation of all sample results reported by the laboratory. Integration reports and chromatograms should be compared to the reported positive sample results.

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3. Verify that the correct RFs are used for quantitation. Verify that the same RFs are used consistently throughout, in both the calibration as well as the quantitation process.

4. Verify that the QLs have been adjusted to reflect all sample dilutions, that are not accounted for by the method.

E. Action

If quantitation limits reported by the laboratory exceed the QAPP-specified quantitation limits, if no sample dilutions were necessary, or if no matrix-related interferences were observed, professional judgment should be used to assess the validity of the elevated sample results. The problem must be noted in the quality assurance review.

If any discrepancies are found, the laboratory may be contacted by the designated representative to obtain additional information that could resolve any differences. If a discrepancy remains unsolved, the reviewer must use professional judgment to decide which value is the best value. Under these circumstances, the reviewer may determine if qualification of data is warranted.

X. FIELD DUPLICATES

A. Review Items

Analytical result forms, chromatograms and integration reports.

B. Objectives

Field duplicate samples may be taken and analyzed as an indication of overall precision. These analyses measure both field and laboratory precision; therefore, the results may have more variability than laboratory duplicates, which measure only laboratory performance. It is also expected that soil duplicate results will have a greater variance than water matrices due to difficulties associated with collecting identical field samples.

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C. Criteria

There are no specific review criteria for field duplicate analyses comparability within the published methods. However, the QAPP should define the field duplicate criteria for solid and aqueous samples as part of the data quality objectives.

D. Evaluation

Samples which are field duplicates must be identified by reviewing the Chain-of-Custody Records or by contacting the client. The reviewer should compare the results reported for each sample and duplicate and calculate the relative percent difference (RPD).

E. Action

Positive results for a target compound should be flagged "L" in the sample and its duplicate if the following criteria are not met:

1. A control limit of ±20% (±40% for solids) for the RPD shall be used for sample values greater than 5× the QL.

2. A control limit of ± 2× the QL shall be used for sample values less than 5× the QL.

XI. SYSTEM PERFORMANCE

A. Review Items

QC summary forms and raw data.

B. Objective

During the period following instrument performance QC checks (e.g., blanks and calibration), changes may occur in the system that degrade the quality of the data. While this degradation would not be directly shown by QC checks until the next required series of analytical QC runs, a thorough review of the ongoing data acquisition can yield indicators of instrument performance.

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C. Criteria

There are no specific criteria for system performance. Professional judgment should be applied to assess the system performance.

D. Evaluation

1. Abrupt, discrete shifts in the chromatogram baseline may indicate a change in the instrument's sensitivity or the baseline setting. A baseline "shift" could indicate a decrease in sensitivity of the instrument or an increase in the instrument baseline, possibly causing target compounds at or near the detection limit to miss detection. A baseline "rise" could indicate problems such as a change in the instrument baseline, a leak or degradation of the column.

2. Poor chromatographic performance affects both qualitative and quantitative results. Indications of substandard performance include:

   a. High background levels or shifts in absolute retention times for calibration standards.

   b. Excessive baseline rise.

   c. Extraneous peaks.

   d. Loss of resolution.

   e. Peak tailing or peak splitting that may result in inaccurate quantitation.

E. Action

Professional judgment must be used to qualify the data if it is determined that system performance has degraded during sample analyses. The data reviewer must use all the information available (surrogate recoveries, MS/MSD analyses, LCSs, etc.) to try to ascertain the effect of baseline or resolution problems which may have occurred during the analysis.

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XII. OVERALL ASSESSMENT OF DATA

A. Review Items

Entire data package, data review results, QAPP, and Sampling and Analysis Plan.

B. Objective

The overall assessment of a data package is a brief narrative in which the data reviewer expresses concerns and comments on the quality and, if possible, the usability of the data.

C. Criteria

Assess the overall quality of the data.

Review all available materials to assess the overall quality of the data, keeping in mind the additive nature of analytical problems.

D. Evaluation

1. Evaluate any technical problems which have not been previously addressed.

2. If appropriate information is available, the reviewer may assess the usability of the data to assist the client in avoiding inappropriate use of the data. Review all available information, including the QAPP, Sampling and Analysis Plan and communications with the client that concerns the intended use and desired quality of these data.

E. Action [illegible]

1. Use professional judgment to determine if there is any need to qualify data which were not qualified based on the QC previously discussed.

2. Prepare a fully documented quality assurance review which provides the client with an indication of the analytical limitations of the data. If sufficient information on the intended use and required quality of the data are available, the reviewer should include his assessment of the usability of the data within the given context.

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SOP approved by:

_____ Date: _____
Rock J. Vitale, CPC
Director of Chemistry

Control Copy No.: _____

Received by: _____

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STANDARD OPERATING PROCEDURES FOR DATA VALIDATION OF VOLATILE ORGANICS BY SW-846 METHOD 8260A*

I. METHOD SUMMARY

Water Samples

The volatile compounds are introduced into the gas chromatography (GC) by the purge-and-trap method or by direct injection (in limited applications). Purged sample components are trapped in a tube containing suitable sorbent materials. When purging is complete, the sorbent tube is heated and backflushed with helium to desorb trapped sample components. The analytes are desorbed directly to a large bore capillary column GC or cryofocussed on a capillary precolumn before being flash evaporated to a narrow bore capillary column GC for analysis. The column is temperature programmed to separate the analytes which are then detected with a mass spectrometer (MS) interfaced to the GC. Wide bore capillary columns require a jet separator, whereas narrow bore capillary columns can be directly interfaced to the ion source.

Soil/Sediment Samples

Low level - an inert gas is bubbled through a mixture of reagent water and 5 gm of sample prior to purging. The analysis then proceeds as described above.

Medium level - a measured amount of soil is extracted with methanol. A portion of the methanol extract is diluted to 5 ml with reagent water. This solution is then subjected to GC/MS analysis following purge and trap, as described above.

II TECHNICAL HOLDING TIMES

A. Review Items

Form I volatile organic analysis (VOA), Chain-of-Custody records, raw data, and Case Narrative

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* See Section XVI for Authority and Application of this SOP.

B. Objective

The objective is to ascertain the validity of results based on the holding time of the sample from the time of collection to the time of analysis.

C. Criteria

Technical requirements for sample holding times have only been established for water matrices. The holding time criteria for water samples are as follows:

- For non-aromatic volatile compounds in cooled (at 4±2°C) water samples, the maximum holding time is 14 days from sample collection.
- For purgeable aromatic hydrocarbons in cooled (at 4±2°C), acid-preserved (pH 2 or below) water samples, the maximum holding time is 14 days from sample collection.
- For purgeable aromatic hydrocarbons in cooled water (4±2°C), samples that have not been preserved to a pH of 2 or below, the maximum holding time is 7 days from sample collection.
- For solid samples, the maximum holding time is 14 days from sample collection.

D. Evaluation Procedure

Technical holding times are established by comparing the sampling dates on the Chain-of-Custody records with the dates of analysis on the VOA Form I's and the raw data. Examine the sample records to determine if samples were preserved.

E. Action

If technical holding times are exceeded, document in the quality assurance (QA) review that holding times were exceeded and qualify the sample results according to the following criteria:

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1. Unpreserved Aqueous Samples:

   a. For aromatic compounds (listed below) in unpreserved (pH>2) water samples analyzed more than 7 days but up to 14 days from sample collection, flag positive aromatic sample results as estimated (flagged "J") and flag "not-detects" as "UJ".

      For non-aromatic compounds in unpreserved (pH>2) samples analyzed more than 14 days but up to 28 days from time of sample collection, flag positive sample results as estimated (flagged "J") and "not-detects" as "UJ".

   b. For aromatic compounds (listed below) in unpreserved (pH>2) water samples analyzed more than 14 days from the date of sample collection, flag all positive results as estimated (flagged "J") and "not-detects" as "R".

      For non-aromatic compounds in unpreserved (pH>2) water samples analyzed more than 28 days from the date of sample collection, flag positive results as estimated (flagged "J") and "not-detects" as "R".

2. Preserved aqueous samples:

   a. For aqueous samples analyzed more than 14 days and less than 28 days from the time of sample collection, flag all positive sample results as estimated (flagged "J") and "not-detects" as "UJ".

   b. For aqueous samples analyzed more than 28 days from the time of sample collection, flag all positive samples results as estimated (flagged "J") and "not-detects" as "R".

3. Solid samples:

   a. For solid samples analyzed more than 14 days and less than 28 days from the time of sample collection, flag all positive sample results as estimated (flagged "J") and "not-detects" as "UJ".

   b. For solid samples analyzed more than 28 days from the time of sample collection, flag all positive samples results as estimated (flagged "J") and not-detects" as "R".

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Aromatic Volatile Compounds

benzene	1,4-dichlorobenzene
chlorobenzene	ethylbenzene
1,2-dichlorobenzene	toluene
1,3-dichlorobenzene	xylenes

4. If a sample is received at the laboratory with a temperature greater than 6°C but less than or equal to 10°C and the temperature of the cooler was measured with an infrared (IR) gun or with a temperature bottle, flag positive results for all compounds as estimated ("J") and all "not-detected" results ("UJ"). In addition, note the deficiency in the QA report.

5. If a sample is received at the laboratory with a temperature greater than 10°C and the temperature of the sample cooler was measured with an IR gun or with a temperature bottle, flag all positive results as estimated ("J") and all "not-detected" results as unusable ("R"). In addition, note the deficiency in the QA report.

6. If high temperatures were noted for project samples, but the laboratory used a method other than temperature bottles or IR guns for measuring the cooler temperatures, comment in the report that high sample temperatures were noted but that the method of measuring the cooler temperature may not reflect actual sample temperatures, and data was not qualified based on this issue. In addition, note if the laboratory indicated the presence of wet ice or "blue ice" in the sample cooler.

III. GC/MS TUNING

A. Review Items

Form V VOA, bromofluorobenzene (BFB) mass spectra, and mass listing

B. Objective

GC/MS tuning is performed to ensure mass resolution, identification, and to some degree, sensitivity. These criteria are not sample-specific and should be met in all circumstances.

C. Criteria

The analysis of the tune must be performed at the beginning of each 12-hour period during which samples or standards are analyzed. The instrument performance check compound, BFB for volatile analysis, must meet the ion abundance criteria given below. Note that alternate tuning criteria (Method 625, Contract Laboratory Program [CLP], etc.) is acceptable as long as method performance is not adversely affected.

BROMOFLUOROBENZENE

m/z	ion abundance criteria
50	15-40% of mass 95
75	30-60% of mass 95
95	base peak, 100% relative abundance
96	5-9% of mass 95
173	less than 2% for mass 174
174	greater than 50% of mass 95
175	5-9% of mass 174
176	greater than 95%, but less than 101% of mass 174
177	5-9% of mass 176

Note: All ion abundances must be normalized to mass 95, the nominal base peak, even though the ion abundance of mass 174 may be greater than that of mass 95.

D. Evaluation

1. Compare the data presented for each tune with each mass listing submitted to ensure the following:

   a. Form V is present and completed for each 12-hour period during which samples were analyzed.

   b. The laboratory has not made transcription errors between the data and the form.

   c. The laboratory has not made calculation errors.

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2. Verify from the raw data that the mass alignment is correct and that the mass listing is normalized to mass 95.

3. Verify that the ion abundance criteria was met. The criteria for mass 173, 175, 176, and 177 are calculated normalizing to the specified mass.

4. All instrument conditions must be identical to those used in the sample analysis.

E. Action

1. If the laboratory has made minor transcription errors, which do not significantly affect the data, the data reviewer should make the necessary corrections on a copy of the form.

2. If the laboratory has failed to provide the correct forms or has made significant transcription or calculation errors, the reviewer must use professional judgment to assess the data.

3. If mass assignment is in error (mass 96 is indicated as the base peak rather than mass 95), qualify all associated data as unusable (flagged "R").

4. If ion abundance criteria are not met, professional judgment may be applied to determine to which extent the data may be utilized. The critical ion abundance criteria for BFB are the mass 95/96, 174/175, 174/176, and 176/177 ratios.

5. Decisions to use analytical data associated with BFB tune not meeting [illegible] requirements should be clearly noted in the QA review.

6. If the reviewer has reason to believe that the tuning criteria were achieved using techniques other than those described, additional information on the tuning should be obtained.

IV. INITIAL CALIBRATION

A. Review Items

Form VI VOA, quantitation reports, and chromatograms

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B. Objective

Compliance requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable qualitative and quantitative data for target compounds.

C. Criteria

1. After the GC/MS tuning and mass calibration, the instrument must be calibrated prior to sample analysis. The initial calibration is performed with at least five standards, one of which should contain each analyte at a concentration at or near the method detection limit (MDL) for that compound; the other calibration standards should contain the analytes at concentrations which define the working range of the instrument. Introduction of the standards into the instrument should be performed in the same manner as will the samples.

2. The average relative response factor (RRF) for each compound must be calculated and recorded using the five RRFs for each compound from the 5-point calibration curve. Five System Performance Check Compounds (SPCCs) are checked for minimum average RRFs. These criteria must be met before samples can be analyzed. If the criteria are not met, the laboratory must correct the problem and recalibrate the instrument.

   The minimum RRF for volatile SPCCs are as follows:

chloromethane	0.10
1,1-dichloroethane	0.10
bromoform	0.10
chlorobenzene	0.30
1,1,2,2-tetrachloroethane	0.30

3. Separate initial calibrations must be performed for aqueous samples (or medium-level soil samples) and for low-level soil samples.

4. The RRFs for all volatile target compounds in the initial calibration should be greater than 0.050.

5. The percent relative standard deviation (% RSD) from the initial calibration must be <30% for each individual calibration check compound (CCC)

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The CCCs are: 1,1-dichloroethene, chloroform, 1,2-dichloropropane, toluene, ethylbenzene, and vinyl chloride.

If a %RSD greater than 30% is measured for any CCC, then corrective action to eliminate a system leak and/or column reactive sites is required before reattempting calibration.

If the %RSD of any compound is 15% or less, then the RRF is assumed to be constant over the calibration range and the average RRF may be used for any quantitation.

If the %RSD of any compound is greater than 15%, the laboratory must construct calibration curves of area ratio (A/A) versus concentration using first or higher order regression fit of the five calibration points.

D. Evaluation

1. Verify that the correct concentrations of standards were used for the initial calibration.

2. Verify that the correct initial calibration was used for aqueous and medium-level soil samples (unheated purge) and for low-level soil samples (heated purge).

3. If any sample results were calculated using an initial calibration, verify that the correct standard (i.e., the 50 µg/l standard) was used for calculating sample results and that the samples were analyzed within 12 hours of the associated tune.

4. Evaluate the initial calibration RRFs for all volatile target compounds.

   a. Check and recalculate the RRFs and average RRFs for at least one volatile target compound associated with each internal standard; verify that the recalculated value(s) agrees with the laboratory-reported value(s). If errors are detected in the calculations, perform a more comprehensive recalculation.

   b. Verify that for all volatile SPCCs, the initial calibration average RRFs are greater than or equal to the proper criteria. In addition, verify that all other compounds display RRFs greater than 0.050.

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5. Evaluate the %RSD for all volatile target compounds.

   a. Check and recalculate the %RSD for one or more volatile target compound(s) and verify that the recalculated value(s) agrees with the laboratory reported value(s). If errors are detected in the calculations, perform a more comprehensive recalculation.

   b. Verify that all volatile target compounds have a %RSD less than or equal to 30.0%.

E. Action

1. If any volatile target compound result has an average RRF of less than 0.050:

   a. Flag positive results for that compound as estimated (flagged "J").

   b. Flag "not-detects" for that compound as unusable ("R").

2. If any volatile target compound has a %RSD greater than 30% and the laboratory used a linear calibration curve or the average RRF for quantitation of a positive result for that compound:

   a. Flag positive results for that compound as estimated (flagged "J").

   b. "Not-detects" for that compound may be qualified using professional judgment.

3. If the initial calibration did not meet all criteria for the CCCs and the SPCCs, note the deficiency in the report. Validate all data based on the criteria stated in E.1. and E.2., above.

V. CONTINUING CALIBRATION

A. Review Items

Form VII VOA, quantitation reports, and chromatograms

B. Objective

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Continuing calibration establishes the 12-hour RRFs on which the quantitations are based and checks satisfactory performance of the instrument on a day-to-day basis.

C. Criteria

1. The initial calibration curve for each compound of interest must be checked and verified once every 12 hours during analysis with the introduction technique used for samples. This is accomplished by analyzing a calibration standard that is at a concentration near the midpoint concentration for the working range of the GC/MS by checking the SPCC and the CCC. A system performance check must be made each 12 hours. If the SPCC criteria are met, a comparison of RRFs is made for all compounds. This is the same check that is applied during the initial calibration. If the minimum RRFs are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins.

2. The continuing calibration RRF for volatile target compounds must be greater than or equal to 0.050.

3. The percent drift between the average initial calibration responses and the concentration of the compounds determined in the continuing calibration must be within the ±20%.

4. Verify that the SPCCs meet all of the RRF criteria as stipulated for the initial calibration.

D. Evaluation Procedure

1. Verify that the continuing calibration was run at the required frequency and that the continuing calibration was compared to the correct initial calibration.

2. Evaluate the continuing calibration RRF for 10% of the volatile target compounds (at least one per internal standard):

   a. Check and recalculate the RRF for at least one volatile target compound associated with each internal standard and verify that the recalculated value(s) agrees with the laboratory-reported value(s). If errors are detected in the calculations of the RRFs, perform a more comprehensive recalculation.

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b. Verify that for all volatile target compounds, the initial calibration average RRFs are > 0.05.

3. Evaluate the % Drift between the responses from the initial calibration and the concentration calculated from the continuing calibration for all compounds.

Calculate the percent drift using the following equation:

$$\% \text{ Drift} = (C_I - C_c) / C_I \times 100$$

where:

C_I = Calibration Check Compound standard concentration.

C_c = Measured concentration using selected quantitation method.

If the % drift for each CCC is less than 20%, the initial calibration is assumed to be valid. If the criterion is not met (>20% drift) for any one CCC, corrective action must be taken. If no source of the problem can be determined after corrective action has been taken, a new five point calibration MUST be generated. This criterion MUST be met before quantitative sample analysis begins. In addition, if the CCCs are not target analytes for the particular analysis, then all target analytes must display % drifts of 20% or less.

E. Action

1. If any volatile compound result has an RRF of less than 0.050:

a. Flag positive results for that compound as estimated (flagged "J").

b. Flag "not-detects" for that compound with an "R".

2. If any volatile target compound has a %D greater than 25.0%:

a. Flag positive results for that compound as estimated (flagged "J").

b. "Not-detects" for that compound may be qualified using professional judgment.

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3. If the continuing calibration failed any of the criteria for the CCCs or SPCCs and the laboratory did not terminate the analysis and recalibrate the instrument, note the deficiency in the QA report. Qualify all data based on the criteria of E.1 and E.2 above.

VI. BLANKS

A. Review Items

Blank Form I VOA, Form IV VOA, chromatograms, and quantitation reports

B. Objective

The assessment of blank analysis results is to determine the existence and magnitude of contamination problems. The criteria for evaluation of blanks apply to any blank associated with the samples. If problems with any blank exist, all associated data must be carefully evaluated to determine whether or not there is an inherent variability in the data, or if the problem is an isolated occurrence not affecting other data. See the Quality Assurance Project Plan (QAPP) for project-specific information regarding field, trip, and equipment blanks.

C. Criteria

1. The method requires only a laboratory blank to be analyzed after a sample analysis which saturates the instrument due to high levels of target or non-target compounds. This blank must be free of interferences or the system must be decontaminated. Samples may not be analyzed until the blank analysis is demonstrated to be free of interferences.

2. Most (if not all) laboratories will analyze a method blank after the continuing calibration and before sample analysis. The method blank should be analyzed on each GC/MS system used to analyze samples for each type of analysis (i.e., unheated purge [aqueous and medium-level solid samples] and heated purge [low-level solid samples]). This method blank should not display target compounds at levels greater than the reporting limits (except for the common laboratory contaminants which should display levels less than five times the reporting limit).

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D. Evaluation Procedure

1. Review the results of all associated blanks on the forms and raw data (chromatograms and quantitation reports) to evaluate the presence of target and non-target compounds in the blanks.

2. Verify that if a sample saturates the instrument, the laboratory followed this analysis with laboratory blanks and these laboratory blanks displayed no interferences.

E. Action

Positive sample results are not qualified for associated blank contamination unless the concentration of the compound in the sample is less than or equal to 10× the amount in any blank for the common volatile laboratory contaminants listed below or 5× the amount for other volatile target compounds. In instances where more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration for a contaminant. The results must not be corrected by subtracting any blank value.

<u>Common Volatile Laboratory Contaminants</u>

methylene chloride

acetone

2-butanone

Specific actions are as follows:

1. If a volatile compound is found in a blank but not found in the sample, no action is taken.

2. If the sample result is greater than the contract required quantitation limit (CRQL) but less than the required amount (5× or 10×) from the blank result, the sample results are qualified as "not-detects" (flagged "U")

3. If the sample result is positive but less than the CRQL and is less than the required amount (5× or 10×) from the blank result, the result is raised to the CRQL and is flagged "U" ("not-detects").

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4. If the sample result is greater than the required amount (5× or 10×) from the blank result, the sample results are not qualified.

5. If gross contamination exists (i.e., saturated peaks by GC/MS), all affected compounds in the associated samples should be qualified as "R" due to interference.

6. The same consideration given to the target compounds should also be given to tentatively identified compounds (TICs) that are found in both the sample and associated blank(s).

VII. SURROGATE RECOVERY

A. Review Items

- Form II VOA, quantitation reports, and chromatograms

B. Objective

Laboratory performance on an individual sample is established by means of spiking activities. All samples are spiked with surrogate compounds prior to sample purging.

C. Criteria

1. Typically, three or four surrogate compounds (1,2-dichloroethane-d_4, [illegible]romethane, bromofluorobenzene, and/or toluene-d_8) are added to the samples and blanks to measure their recovery in environmental samples in sample and blank matrices.

2. Recoveries for surrogate compounds in volatile samples and blanks should be within the limits specified below. If not, the laboratory must reextract (medium-level analysis) and reanalyze the samples.

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SURROGATE COMPOUND CRITERIA

Surrogate	Water %R	Solid %R
toluene-d_8	88-110	81-117
bromofluorobenzene	86-115	74-121
1,2-dichloroethane-d_4	80-120	80-120
dibromofluoromethane	86-118	80-120

D. Evaluation Procedure

1. Check raw data (i.e., chromatograms and quantitation reports) to verify the recoveries on the surrogate recovery form II. Check for any calculation or transcription errors.

2. The following should be determined from the Surrogate Recovery Form(s):

   a. If any surrogate compound in the volatile fraction is out of specification, there should be a reanalysis to confirm that the noncompliance is due to sample matrix effects rather than laboratory deficiencies.

   b. The laboratory failed to perform appropriately if surrogate compounds are outside criteria with no evidence of re-analysis.

   c. Verify that no blanks have surrogate compounds outside the criteria.

E. Actions

Data are qualified based on surrogate compound results if the recovery of any volatile surrogate compound is out of specification. For surrogate compound recoveries out of specification, the following approaches are suggested:

1. If any surrogate compound in the volatile sample has a recovery greater than the upper acceptance limit:

   a. Positive results for volatile target compounds are qualified as estimated (flagged "J").

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b. "Not-detected" results for volatile target compounds should not be qualified.

2. If a surrogate compound in the volatile sample has a recovery greater than or equal to 10% but less than the lower acceptance limit:

   a. Positive volatile target compounds are qualified as estimated (flagged "J").

   b. Results for "not-detected" volatile target compounds should be qualified "UJ".

3. If a surrogate compound in the volatile sample has a recovery less than 10%:

   a. Positive volatile target compounds are qualified as estimated (flagged "J").

   b. Results for "not-detected" volatile target compounds should be qualified "R".

4. If, upon re-analysis, the recovery is again not within limits, flag the data as estimated (flagged "J" or "UJ").

VIII. MATRIX SPIKE/MATRIX SPIKE DUPLICATES

A. Review Items

Form III, chromatograms, and quantitation reports

B. Objective

Data for matrix spike/matrix spike duplicates are generated to determine long-term precision and accuracy of the analytical method on various matrices and demonstrate acceptable compound recovery by the laboratory at the time of sample analysis. These data alone are used to evaluate the precision and accuracy of other samples.

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b. "Not-detected" results for volatile target compounds should not be qualified.

2. If a surrogate compound in the volatile sample has a recovery greater than or equal to 10% but less than the lower acceptance limit:

   a. Positive volatile target compounds are qualified as estimated (flagged "J").

   b. Results for "not-detected" volatile target compounds should be qualified "UJ".

3. If a surrogate compound in the volatile sample has a recovery less than 10%:

   a. Positive volatile target compounds are qualified as estimated (flagged "J").

   b. Results for "not-detected" volatile target compounds should be qualified "R".

4. If, upon re-analysis, the recovery is again not within limits, flag the data as estimated (flagged "J" or "UJ").

VIII. MATRIX SPIKE/MATRIX SPIKE DUPLICATES

A. Review Items

Form III, chromatograms, and quantitation reports

B. Objective

Data for matrix spike/matrix spike duplicates are generated to determine long-term precision and accuracy of the analytical method on various matrices and demonstrate acceptable compound recovery by the laboratory at the time of sample analysis. These data alone are used to evaluate the precision and accuracy of other samples.

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C. Criteria

Matrix spike and matrix spike duplicate samples should be analyzed at a frequency of one matrix spike and matrix spike duplicate per 20 samples per analytical batch. It should be noted that an matrix spike/matrix spike duplicate analysis is not required by Method 8260A. Refer to the QAPP for project-specific requirements for the matrix spike/matrix spike duplicate.

D. Evaluation

1. Verify transcriptions from raw data and verify calculations.

2. Compare %RSD results of nonspiked compounds for the unspiked sample and the matrix spike and matrix spike duplicate samples.

3. Verify that all observed recoveries for the spiked compounds are within the reported criteria. In addition, verify that the percent differences for the spiked compounds are less than the reported quality control criteria.

E. Action

1. No action is taken on MS/MSD data alone. However, using informed professional judgment, the data reviewer may use the matrix spike and matrix spike duplicate results in conjunction with the other QC criteria and determine the need for some qualification of the data.

2. In the instance where it can be determined that the results of the matrix spike/matrix spike duplicate affect only the sample spiked, then the following criteria should be used for the sample that was spiked:

   a. If the recovery of a matrix spike compound in the volatile matrix spike and/or matrix spike duplicate has a recovery greater than the reported upper acceptance limit (or 130%, whichever is more strict), positive results for that compound in the unspiked sample should be considered estimated (flagged "J").

   b. If the recovery of a matrix spike compound in the volatile matrix spike and/or matrix spike duplicate has a recovery less than 69% (or the laboratory's lower reporting limit, whichever is more strict) and greater than 31%, the positive result for that compound in the

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unspiked sample should be considered estimated (flagged "J" or the "not-detected" result should be flagged "UJ").

c. If the recovery of a matrix spike compound in the volatile matrix spike and/or matrix spike duplicate has a recovery less than 30%, "not-detected" results should be flagged "R".

d. If matrix spike/matrix spike duplicate pairs exceed the specified relative percent difference (RPD) (20%; aqueous and 40% solid), positive results for that compound should be considered estimated (flagged "J").

3. If the RPD between results for unspiked compounds in the MS/MSD exceeds 20% for aqueous samples (40% for solid samples) and all results in the matrix spike/matrix spike duplicate and unspiked sample are greater than 5× the reporting limit, flag the positive result in the unspiked sample as estimated ("J").

4. If the range of results for unspiked compounds among the matrix spike/matrix spike duplicate and unspiked aqueous sample exceeds the CRQL (2×CRQL for solid samples) and at least one of the results is less than 5× the CRQL, flag the positive result for the unspiked compounds as estimated ("J").

IX. LABORATORY CONTROL SAMPLES (LCS)

A. Requirements

LCS summary forms, quantitation reports, and chromatograms

B. Objective

To establish and document the laboratory's ability to generate acceptable precision and accuracy for each target compound in the analysis.

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C. Criteria

1. The laboratory is required to analyze four aliquots of the LCS to demonstrate acceptable performance as displayed by the recoveries and standard deviations for the target compounds. The frequency of the LCS analysis is not stipulated in the method; it is recommended that one series of LCS analyses is performed per batch of samples or per 20 samples, whichever is more frequent.

2. The recoveries for the target compounds must be within the range $\bar{x} \pm 30\%$ or $\bar{x} \pm 3s$, whichever is greater (the values for $\bar{x}$ and s can be found in Table 6 for wide-bore capillary columns and Table 7 for narrow-bore capillary columns).

3. The RSDs for all target compounds for the four LCS analyses must be less than 20% or 2.6×RSD as given in Table 6 and Table 7 of the method.

4. If either the %RSD or recovery criteria is not met for any compound, the laboratory must perform one of the corrective actions:

   a. The laboratory may reanalyze four LCS aliquots and report the results for all target compounds.

   b. The laboratory may reanalyze four LCS aliquots and report only the results for the target compounds which failed the %RSD or recovery criteria in the first series of LCS analyses. However, if failing %RSDs or recoveries are again observed, the laboratory must reanalyze four LCS aliquots for <u>all</u> target compounds.

5. It should be noted that site-specific QAPPs may stipulate criteria for the frequency, %RSDs, recoveries, and corrective actions for the LCS analyses which are different than those stated in the method. In such cases, determine laboratory performance based on the requirements of the QAPP rather than the method.

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D. Evaluation

1. Verify the transcriptions from the raw data to the summary forms. Recalculate 10% of the reported results (concentrations, recoveries, and RSDs) to verify that the results were quantitated correctly.

2. Verify that all recoveries for all target compounds are within the ranges stipulated above.

3. Verify that all RSDs are less than the limits provided in the method for the target compounds.

4. If any of the recoveries or RSDs in the LCS analysis exceeded the stated limits, verify that the laboratory either reanalyzed the LCS for all target compounds or reanalyzed the LCS for only those compounds which displayed unacceptable results. If the laboratory performed the latter, and failing LCS results were again observed, verify that the laboratory then reanalyzed the LCS for all target compounds.

E. Action

The results for the LCS analysis are used to qualify data for all samples associated with the LCS. If more than one series of LCS analyses are performed for one SDG, use the analysis run logs and sample preparation logs (if provided) to determine which samples are associated with which LCS analysis.

1. If unacceptable recoveries and/or RSDs were observed for any target compound in the LCS analysis and the laboratory did not perform the corrective action as required, include a note of this deficiency in the QA report.

2. If extensive transcription errors or missing data is noted during the review of the data package, the laboratory should be contacted to provide the missing data or resubmit corrected forms.

3. If at least one recovery (out of four LCS aliquot analyses) for a target compound is outside the stated criteria ($\bar{x} \pm 3s$ or $\bar{x} \pm 30\%$, whichever is greater), flag all positive results for that compound in all associated samples as estimated ("J").

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4. If at least one recovery for a target compound is less than $\bar{x}$-3s or $\bar{x}$-30%, whichever is less, but greater than or equal to 30%, flag all "not-detected" results for the compound in the associated samples as estimated ("UJ").

5. If at least one recovery for a target compound is less than 30%, flag all "not-detected" results for the compound in all associated samples "R" and the analysis for the compound in all associated samples should be considered unusable.

6. "Not-detected" results for compounds displaying high recoveries in the LCS analysis are not necessarily qualified.

7. If a target compound displays a high RSD (greater than 20% or 2.6× the RSD stipulated in the method), flag positive results for the compound in all associated samples as estimated ("J"). "Not-detected" results are not necessarily qualified due to high RSDs observed in the LCS analysis.

X. INTERNAL STANDARDS

A. Review Items

Form VIII, quantitation reports, and chromatograms

B. Objective

Internal standards performance criteria ensure that GC/MS sensitivity and response is stable during every analysis.

C. Criteria

1. Every standard sample and blank must be spiked with internal standard compounds. Recommended internal standards are fluorobenzene, chlorobenzene-d_5, and 1,4-dichlorobenzene-d_4.

2. Internal standard area counts in the continuing calibration must not vary by more than a factor of two (-50% to +100%) from the previous continuing calibration standard or initial calibration standard of the same concentration.

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3. The retention times of the internal standards in the continuing calibration must not vary more than ±30 seconds from the previous continuing calibration standard or the initial calibration standard of the same concentration.

4. If a continuing calibration standard displays unacceptable retention times or area counts for one or more internal standards, the laboratory must correct the problem, reanalyze the continuing calibration standard, and reanalyze all samples associated with the failing continuing calibration standard.

5. It should be noted that the aforementioned retention time and area count requirements apply only to the continuing calibration standard. The method does not require reanalysis for samples which display unacceptable retention times or area counts for the internal standards. However, most laboratories will reanalyze samples with unacceptable internal standard responses to verify matrix effects. In addition, site-specific QAPPs will often state requirements for the responses for internal standards in the project samples.

D. Evaluation Procedure

1. Check raw data (e.g., chromatograms and quantitation lists) to verify the internal standard retention times and areas reported on the Internal Standard Area Summary Forms (Form VIII VOA).

2. Verify that all retention times and internal standard areas are within criteria.

3. If there are two analyses for a particular fraction, the reviewer must determine which are the best data to report. Considerations should include:

   a. Magnitude and direction of the internal standard area shift.

   b. Magnitude and direction of the internal standard retention time shift.

   c. Technical holding times.

   d. Comparison of the values of the target compounds reported in each fraction.

e. Other quality control (QC) data results.

E. Action

1. If an internal standard area count for a sample or blank is outside -50% or +100% of the area for associated standard:

   a. Positive results for compounds quantitated using that internal standard should be qualified as estimated (flagged "J").

   b. "Not detected" results reported using an internal standard area count less than -50% or greater than +100% are reported as the associated quantitation limit and qualified "UJ".

   c. If extremely low area counts are reported (<25%), or if performance exhibits a major abrupt drop-off, then a severe loss of sensitivity is indicated. "Not detected" target compounds should then be qualified as unusable (flagged "R").

2. If an internal standard retention time varies by more than 30 seconds, the chromatographic profile for that sample must be examined to determine if any false positives or negatives exist. For shifts of a large magnitude, the reviewer may consider partial or total rejection of that data for that sample fraction. Positive results should not need to be qualified as "R" if the mass spectral criteria are met.

XI. TARGET COMPOUND IDENTIFICATION

A. Review Items

Form I, quantitation reports, mass spectra, and chromatograms

B. Objective

The objective of the criteria for GC/MS qualitative analysis is to minimize the number of erroneous identifications of compounds. An erroneous identification can either be a false positive (reporting a compound present when it is not) or a false negative (not reporting a compound that is present).

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C. Criteria

1. The relative retention times (RRTs) must be within ±0.06 RRT units of the standard RRT.

2. Mass spectra of the sample compound and a current laboratory-generated standard (i.e., the mass spectrum from the associated calibration standard) must match according to the following criteria:

   a. All ions present in the standard mass spectrum at a relative intensity greater than 10% must be present in the sample spectrum.

   b. The relative intensities of these ions must agree within ±30% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 20% and 80%).

D. Evaluation Procedures

1. Verify that the RRT of reported compounds is within ±0.06 RRT units of the standard RRT.

2. Check the sample compound spectra against the laboratory standard spectra to see that it meets the specified criteria.

3. The reviewer should be aware of situations (e.g., high concentration samples preceding low concentration samples) when sample carryover is a possibility and should use judgment to determine if instrument cross-contamination has affected any positive compound identification.

4. Check the chromatogram to verify that peaks are accounted for (i.e., major peaks are either identified as target compounds, tentatively identified compounds (TICs), surrogates, or internal standards).

E. Action

1. The application of qualitative criteria for GC/MS analysis of target compounds requires professional judgment. If it is determined that incorrect identifications were made, all such data should be qualified as "not-detected" (flagged "U") or unusable (flagged "R").

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2. Professional judgment must be used to qualify the data if it is determined that cross-contamination has occurred.

XII. COMPOUND QUANTITATION AND REPORTED CRQLs

A. Review Items

Form I, Case Narrative, quantitation reports and chromatograms.

B. Objective

The objective is to ensure that the reported quantitation results and CRQLs are accurate.

C. Criteria

1. Compound quantitation, as well as the adjustment of the CRQLs, must be calculated according to the correct equation specified in the analytical protocol.

2. Compound RRF must be calculated based on the internal standard (IS) specified in the analytical protocol for that compound. Quantitation must be on the quantitation ion (m/z) specified in the analytical protocol. The compound quantitation must be based on the RRF from the associated daily standard.

D. Evaluation Procedure

1. Verify that method quantitation limits reported by the laboratory are less than or equal to the CRQLs. If sample dilution is necessary due to elevated target compound concentrations, or if interference related to the sample matrix is observed, method quantitation limits reported by the laboratory may exceed required limits.

2. For all fractions, raw data should be examined to verify the correct calculation of all sample results reported by the laboratory. Quantitation lists and chromatograms should be compared to the reported positive sample results and quantitation limits.

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3. Verify that the correct IS, quantitation ion, and RRF were used to quantitate the compound. Verify that the same IS, quantitation ion, and RRF are used consistently throughout, in both the calibration, as well as the quantitation process.

4. Verify that the CRQLs have been adjusted to reflect all sample dilutions and dry weight factors that are not accounted for by the method.

E. Action

If method quantitation limits reported by the laboratory exceed corresponding project required quantitation limits and no sample dilutions were necessary or matrix-related interference observed, professional judgment should be used to assess the validity of the elevated sample results. The problem should be noted in the QA review.

If any discrepancies are found, the laboratory may be contacted by the designated representative to obtain additional information that could resolve any differences. If a discrepancy remains unsolved, the reviewer must use professional judgment to decide which value is the best value. Under these circumstances, the reviewer may determine if qualification of data is warranted.

VIII. FIELD DUPLICATE

A. Review Items

Forms, chromatograms, and quantitation reports

B. Objective

Field duplicate samples may be taken and analyzed as an indication of overall precision. These analyses measure both field and laboratory precision; therefore, the results may have more variability than laboratory duplicates which measure only laboratory performance. It is also expected that soil duplicate results will have a greater variance than water matrices due to difficulties with collecting identical field samples.

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3. Verify that the correct IS, quantitation ion, and RRF were used to quantitate the compound. Verify that the same IS, quantitation ion, and RRF are used consistently throughout, in both the calibration, as well as the quantitation process.

4. Verify that the CRQL's have been adjusted to reflect all sample dilutions and dry weight factors that are not accounted for by the method.

E. Action

If method quantitation limits reported by the laboratory exceed corresponding project required quantitation limits, and no sample dilutions were necessary or matrix-related interference observed, professional judgment should be used to assess the validity of the elevated sample results. The problem should be noted in the QA review.

If any discrepancies are found, the laboratory may be contacted by the designated representative to obtain additional information that could resolve any differences. If a discrepancy remains unsolved, the reviewer must use professional judgment to decide which value is the best value. Under these circumstances, the reviewer may determine if qualification of data is warranted.

XIII. FIELD DUPLICATE

A. Review Items

Form I, chromatograms, and quantitation reports

B. Objective

Field duplicate samples may be taken and analyzed as an indication of overall precision. These analyses measure both field and laboratory precision; therefore, the results may have more variability than laboratory duplicates which measure only laboratory performance. It is also expected that soil duplicate results will have a greater variance than water matrices due to difficulties with collecting identical field samples.

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C. Criteria

There are no specific review criteria for field duplicate analyses comparability. Refer to the site QAPP for project-specific requirements for sampling frequency and RPDs.

D. Evaluation Procedure

Samples which are field duplicates should be identified. The reviewer should compare the results reported for each sample and duplicate and calculate the RPD.

E. Action

Positive results for a target compound should be flagged "J" in the sample and its duplicate if the following criteria are not met.

1. A control limit of ±20% (40% for solids) for the RPD shall be used for sample values greater than 5× the CRQL.

2. A control limit of ± the CRQL (2× the CRQL for solids) shall be used for sample values less than 5× the CRQL.

XIV. SYSTEM PERFORMANCE

A. Review Items

For VTI VOA, Form III VOA, and chromatograms

B. Objective

During the period following instrument performance QC checks (e.g., blanks, tuning, calibration), changes may occur in the system that degrade the quality of the data. While this degradation would not be directly shown by QC checks until the next required series of analytical QC runs, a thorough review of the on-going data acquisition can yield indicators of instrument performance.

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C. Criteria

There is no specific criteria system for performance. Professional judgment should be applied to assess the system performance.

D. Evaluation Procedure

1. Abrupt, discrete shifts in the reconstructed ion chromatogram (RIC) baseline may indicate a change in the instrument's sensitivity or the zero setting. A baseline "shift" could indicate a decrease in sensitivity in the instrument or an increase in the instrument zero, possibly causing target compounds at or near the detection limit, to miss detection. A baseline "rise" could indicate problems such as a change in the instrument zero, a leak, or degradation of the column.

2. Poor chromatographic performance affects both qualitative and quantitative results. Indications of substandard performance include:

   a. High RIC background levels or shifts in absolute retention times of internal standards.

   b. Excessive baseline rise at elevated temperature.

   c. Extraneous peaks.

   d. Loss of resolution.

   e. Peak tailing or peak splitting that may result in inaccurate quantitation.

E. Action

Professional judgment must be used to qualify the data if it is determined that system performance has degraded during sample analyses.

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XV. OVERALL ASSESSMENT OF DATA

A. Review Items

Entire data package, data review results and, if available, QAPP and Sampling and Analysis Plan

B. Objective

The overall assessment of a data package is a brief narrative in which the data reviewer expresses concerns and comments on the quality and, if possible, the usability of the data.

C. Criteria

Assess the overall quality of the data.

Review all available materials to assess the overall quality of the data, keeping in mind the additive nature of analytical problems.

D. Evaluation Procedure

1. Evaluate any technical problems which have not been previously addressed.

2. If appropriate information is available, the reviewer may assess the usability of the data to assist the data user in avoiding inappropriate use of the data. Review all available information, including the QAPP, Sampling and Analysis Plan, and communication with the data user that concerns the intended use and desired quality of these data.

E. Action

1. Use professional judgment to determine if there is any need to qualify data which were not qualified based on the QC previously discussed.

2. Write a brief narrative to give the user an indication of the analytical limitations of the data. If sufficient information on the intended use and required quality of the data are available, the reviewer should include an assessment of the usability of the data within the given context.

XVI. AUTHORITY

This data validation SOP for the analysis for volatile organic compounds by GC/MS (SW-846 Method 8260A) has been prepared by Environmental Standards, Inc. This SOP represents internal control copy _____ issued to and is not to be photocopied or used by any other entity except Environmental Standards, Inc. without expressed written permission.

SOP approved by:

_____ Date:
Rock J. Vitale, CPC
Technical Director of Chemistry/Principal

Control Copy No.:

Received by:

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STANDARD OPERATING PROCEDURES FOR THE DATA VALIDATION OF SEMIVOLATILE ORGANIC COMPOUNDS BY GC/MS (SW-846, METHOD 8270B)*

I. INTRODUCTION

This method is used to determine a wide range of semivolatile organic compounds including most neutral, acidic, and basic organic compounds which are soluble in methylene chloride. Typically, this method is used to analyze for target compound list (TCL), Priority Pollutant List (PPL), and Appendix IX semivolatile compounds. However, this method may also be used for the analysis of additional polynuclear aromatic hydrocarbons (PAHs), chlorinated hydrocarbons, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehyde ethers, ketones, amines, pyridines, quinolines, aromatic nitro compounds, phenols, pesticides, herbicides, insecticides, and polychlorinated biphenyls (PCBs).

This method is applicable for the analysis of extracts from aqueous, soil, and solid waste matrices. Samples are extracted using methylene chloride or other appropriate solvents and concentrated prior to injection into the gas chromatograph/mass spectrometer (GC/MS) for separation and detection of individual compounds. Sample concentrations are determined using internal standard methods. Interferences due to inherent sample matrix contents may affect qualitative and quantitative determinations, and sample extracts may require cleanup prior to analysis. The compounds *alpha*-BHC, *gamma*-BHC, endosulfan I, endosulfan II, and N-nitrosodiphenylamine are known to decompose during analysis. Several chlorinated and nitro substituted phenols and anilines are subject to erratic chromatographic behavior.

Method 8270B is subject to laboratory interpretations of analytical and quality control (QC) procedures and criteria. In addition, the project-specific Quality Assurance Project Plan (QAPP) may include requirements which differ from those presented in the standard operating procedure (SOP). Therefore, professional judgment must be used when applying the contents of the SOP to all situations.

* See Section XVIII for the Authority and Application of this SOP.

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II. TECHNICAL HOLDING TIMES

A. Review Items

Form I SV or equivalent, Chain-of-Custody records, raw data, sample extraction logs, Case Narrative, and Laboratory Sample Log-in documentation

B. Objective

The objective is to ascertain the validity of results based on the holding time of the sample from the time of collection to the time of extraction and analysis.

C. Criteria

The holding time criteria for semivolatile compounds in cooled (4±2°C) water samples is 7 days from sample collection to extraction and 40 days from sample extraction to analysis. Aqueous samples submitted for semivolatile analysis are typically contained in 1 liter amber glass containers with a Teflon®-lined lid at 4°C.

The holding time criteria for semivolatile compounds in non-aqueous samples (sediments, sludge, soils, and solids) is 14 days from sample collection to extraction and 40 days from sample extraction to analysis. Soil samples submitted for semivolatile analysis are typically contained in 250 ml, widemouth, glass jars with Teflon®-lined lids at 4±2°C. Waste samples may be submitted in 125 ml jars. Waste samples do not require temperature preservation.

D. Evaluation

Technical holding times are established by comparing the sampling dates on the Chain-of-Custody records with the dates of extraction and analysis on the Semivolatile Form I's, the sample extraction logs, and the raw data. Verify that the samples were extracted and analyzed within the holding times specified above. Examine the Chain-of-Custody records and Laboratory Sample Log-in documentation to determine if samples were preserved.

E. Action

If technical holding times were exceeded, document in the quality assurance (QA) review that holding times were exceeded from those specified in Chapter 4, Table 4-1 of SW-846, and qualify the sample results according to the following criteria:

1. For aqueous sample extraction:

   a. If extraction of aqueous samples was performed more than 7 days but up to 14 days from the date of sample collection, flag positive results as estimated (flagged "J") and "not-detects" as "UJ".

   b. If extraction of aqueous samples was performed more than 14 days from the date of collection, flag positive results as estimated (flagged "J") and "not-detects" as "R".

2. For aqueous sample analysis:

   a. If aqueous samples were analyzed more than 40 days but up to 80 days from the date of sample extraction, flag positive results as estimated (flagged "J") and "not-detects" as "UJ".

   b. If aqueous samples were analyzed more than 80 days from the date of sample extraction, flag positive results as estimated (flagged "J") and "not-detects" as "R".

3. For solid and waste sample extraction:

   a. If solid samples were extracted more than 14 days but up to 28 days from the date of sample collection, flag positive results "J" and "not-detects" as "UJ".

   b. If extraction of solid samples was performed more than 28 days from the date of collection, flag positive results as estimated (flagged "J") and "not-detects" as "R".

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4. For solid and waste sample analysis:

   a. If solid samples were analyzed more than 40 days but less than 80 days from the date of sample extraction, flag positive results as estimated (flagged "J") and "not-detects" as "UJ".

   b. If solid samples were analyzed more than 80 days from the date of sample extraction, flag positive results as estimated (flagged "J") and "not-detects" as "R".

5. If aqueous and soil samples were not received at the proper temperature of 4±2°C based on the review of the Chain-of-Custody records, laboratory sample receipt records, and/or the narrative, the following determination must be made prior to the qualification of the data:

   If the temperature of the samples was measured by placing the thermometer or probe between the bottles, taking the air temperature in the cooler, or by placing the thermometer in any free liquid in the cooler due to melting ice, no qualification of data is performed. However, a comment in the validation report should note the temperature recorded, the method of measurement, if ice was present upon laboratory receipt, and that there is no direct impact on the usability of the data.

   b. If the temperature of the samples was based upon the measured temperature of the temperature bottle blank or using an infrared (IR) gun, the following qualifications are warranted:

   If the temperature of the temperature bottle upon receipt at the laboratory was greater than 6°C but <10°C, a comment will be written in the data validation report addressing the fact that elevated temperatures may lead to a loss of analyte; however, the data reviewer has not considered the data to have been impacted due to the stability and chemical properties (i.e., vapor pressure, boiling point, etc.) of the semivolatile compounds.

   If aqueous soil samples were not received at the proper temperature of 4±2°C, flag positive results as estimated (flagged "J") and "not-detects" as "UJ" if the samples were received at >10°C but ≤20°C.

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If received at >20°C, flag positives as estimated (flagged "J") and "not-detects" as "R".

c. Waste samples are not qualified based on temperature issues.

III. GC/MS TUNING

A. Review Items

Form V SV or equivalent, decafluorotriphenylphosphine (DFTPP) mass spectra, and mass listing.

B. Objective

GC/MS tuning is performed to ensure mass resolution, identification, and to some degree, sensitivity. These criteria are not sample specific and should be met in all circumstances.

C. Criteria

The analysis of a 50 ng injection (1 µl) of the GC/MS tuning standard solution must be performed at the beginning of each 12-hour period during which samples or standards are analyzed. The GC/MS tuning standard, DFTPP for semivolatile analysis, must meet the ion abundance criteria given below:

DFTPP CRITERIA

m/z	ion abundance criteria
51	30-60% of m/z 198
68	less than 2% of m/z 69
70	less than 2% of m/z 69
127	40-60% of m/z 198
197	less than 1% of m/z 198
198	base peak, 100% relative abundance
199	5-9% of m/z 198
275	10-30% of m/z 198
365	greater than 1% of m/z 198
441	present, but less than m/z 443
442	greater than 40% of m/z 198
443	17-23% of m/z 442

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Note: All ion abundances must be normalized to m/z 198, the nominal base peak, even though the ion abundance of m/z 442 may be greater than that of m/z 198. In addition, Method 8270B allows for alternate tuning criteria (i.e., CLP, Method 525, etc.) as long as method performance is not adversely affected.

The GC/MS tuning standard should also be used to assess GC column performance and injection port inertness. The GC/MS tuning standard, in addition to DFTPP, should contain 50 ng/µl of 4,4'-DDT, pentachlorophenol, and benzidine. The degradation of 4,4'-DDT to DDE and DDD should not exceed 20%. Benzidine and pentachlorophenol should be present at responses (area counts) similar to those obtained in the subsequent calibration, peak tailing should not be visible. Many laboratories have interpreted this portion of the GC/MS tuning procedure to be optional.

D. Evaluation

1. Compare the data presented for each tune (Form V SV) with each mass listing submitted to verify the following:

   a. Form V SV is present and completed for each 12-hour period during which samples were analyzed.

   b. The laboratory has not made transcription errors between the data and the form.

   c. The laboratory has not made calculation errors.

2. Verify from the raw data that the mass alignment is correct and that the base peak is normalized to m/z 198.

3. Verify that the ion abundance criteria was met. The criteria for m/z 68, 70, 441, and 443 are calculated normalizing to the specified m/z.

4. All instrument conditions must be identical to those used in the sample analysis.

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E. Action

1. If the laboratory has made minor transcription errors which do not significantly affect the data, the data reviewer should make the necessary corrections on a copy of the form.

2. If the laboratory has failed to provide the correct forms or has made significant transcription or calculation errors, the reviewer must use professional judgment to assess the data.

3. If mass assignment is in error (such as m/z 199 is indicated as the base peak rather than m/z 198), qualify all associated data as unusable (flagged "R").

4. If the abundance criteria are not met, professional judgment may be applied to determine to what extent the data may be utilized. The critical ion abundance criteria for DFTPP are the m/z 198/199 and 442/443 ratios. If the laboratory used an alternate method criteria instead, note this as a comment in the QA review and evaluate the tuning against the alternate criteria.

5. Decisions to use analytical data associated with DFTPP tunes not meeting method requirements should be clearly noted in the QA review.

6. If the reviewer has reason to believe that the tuning criteria were achieved using techniques other than those described, additional information on the tuning should be obtained.

7. If the column performance portion of the GC/MS tuning procedure is followed by the laboratory, verify that the percent breakdown of 4,4'-DDT is less than 20%. The following calculation is used:

$$\% \text{ breakdown of } 4,4' - \text{DDT} = \frac{\text{total DDT degradation peak areas } (\text{DDE} + \text{DDD})}{\text{peak areas } (\text{DDT} + \text{DDE} + \text{DDD})}$$

Review the benzidine and pentachlorophenol peaks on the chromatogram to determine if peak shape and areas or height of the peaks to the subsequent calibration standard are similar. A ratio approach if the standard concentration is different that the 50 ng/µl concentration in the GC/MS tuning standard.

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If the 4,4'-DDT exceeds 20% degradation or poor peak shape problems are noted, the data reviewer should note this in the report and use professional judgment to determine the effect on the sample data.

IV. INITIAL CALIBRATION

A. Review Items

Form VI SV or equivalent, quantitation reports, and chromatograms.

B. Objective

Compliance requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable qualitative and quantitative data for the semivolatile compounds.

C. Criteria

1. A 1 µl aliquot of each initial calibration standard containing all semivolatile target compounds, internal standards, and surrogate compounds are analyzed at a minimum of five concentrations at the beginning of each analytical sequence or as necessary, if the continuing calibration acceptance criteria are not met. One of the calibration standards should be at a concentration slightly above the laboratory-determined method detection limits (MDLs). Internal standard compounds are injected into the calibration standards prior to analysis. The initial calibration and any associated samples and blanks must be analyzed within 12 hours of the [illegible] tune.

2. Method criteria state that a minimum <u>average</u> relative response factor (RRF) of 0.050 must be met for the system performance check compounds (SPCCs): 2,4-dinitrophenol; *N*-nitroso-di-*n*-propylamine; hexachlorocyclopentadiene; and 4-nitrophenol. However, for determining data usability, <u>any</u> initial calibration RRF must be ≥ 0.050.

3. Method criteria state that the percent relative standard deviation (%RSD) of the RRFs should be less than 15% for each compound. If the %RSD of any compound is < 15%, then the RRF is assumed to be constant over the calibration range and the average RRF may be used for quantitation If the %RSD for any compound is greater than 15%, calibration curves of area

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ratios (area of compound/area of internal standard) versus concentration using first or second order regression are constructed. The use of these regression curves is a recommended alternative to average RRF calibration. As an additional requirement, the %RSD of the relative response factors for each individual calibration check compound (CCC) must be less than 30%. The CCCs are listed in the following table:

Base/Neutral Fraction	Acid Fraction
acenaphthene	4-chloro-3-methylphenol
1,4-dichlorobenzene	2,4-dichlorophenol
hexachlorobutadiene	2-nitrophenol
N-nitrosodiphenylamine	phenol
di-*n*-octyl phthalate	pentachlorophenol
fluoranthene	2,4,6-trichlorophenol
benzo(a)pyrene	

If any CCC displays a %RSD > 30%, the laboratory must correct the problem and repeat the initial calibration sequence. However, for determining data usability, the %RSD from the initial calibration must be ≤ 30% for all target compounds.

4. The relative retention times of each compound in each calibration analysis should agree within 0.06 relative retention time units.

D. Evaluation

1. Verify that the correct concentrations of standards were used for the initial calibration and that the low concentration standard is near the MDL.

2. Verify that the correct initial calibration was used for all samples.

3. If any sample results were calculated using an initial calibration, verify that the average RRF was used for calculating sample results and that the samples were analyzed within 12 hours of the associated tune.

4. Evaluate the initial calibration RRFs for all semivolatile target compounds.

   a. Check and recalculate the RRFs and average RRFs for at least one semivolatile target compound associated with each internal standard; verify that the recalculated value(s) agrees with the

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laboratory reported value(s). If errors are detected in the calculations, perform a more comprehensive recalculation.

b. Verify that for all semivolatile target compounds and surrogates, all initial calibration RRFs are ≥ 0.050.

5. Evaluate the %RSD for all semivolatile target compounds.

a. Check and recalculate the %RSD for one or more semivolatile target compound(s); verify that the recalculated value(s) agrees with the laboratory reported value(s). If errors are detected in the calculations, perform a more comprehensive recalculation.

b. Verify that all semivolatile target compounds have a %RSD ≤30%.

6. Evaluate relative retention times for several compounds to verify retention time agreement of 0.06 RRT units.

7. Verify that the internal standard assigned to each analyte for calculation of RRFs is consistent with Table 5 in SW-846 Method 8270B.

E. Action

1. If any semivolatile target compound result has any RRFs of less than 0.050:

a. Flag positive results for that compound as estimated (flagged "J").

b. Flag "not-detects" for that compound with an "R".

2. If any semivolatile target compound has a %RSD greater than 30%:

a. Flag positive results for that compound as estimated (flagged "J").

b. Flag positive results as estimated (flagged "J") and "not-detects" as "UJ" for any compound with a %RSD of >50%.

c. Flag positive results as estimated (flagged "J") and "not-detects" as "R" for any compound with a %RSD of > 90%.

d. Functional Guidelines (2/94) also suggests eliminating either the high point or the low point to restore the % RSD to ≤ 30%, in

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which case, only positive results greater than the "new linear range" are flagged "J" or only positive results in the area of nonlinearity are flagged "J".

3. If the assignment of the internal standards does not match Table 5 in SW-846, a non-correctable deficiency should be included in the data validation report. However, for non-SPCC and non-CCC compounds, this issue should have no impact on data quality, as long as the same internal standard is used for that compound for all subsequent continuing calibrations.

V. CONTINUING CALIBRATION

A. Review Items

Form VII or equivalent, quantitation reports, and chromatograms

B. Objective

Continuing calibrations are analyzed to monitor calibration and compound response drift and checks satisfactory performance of the instrument on a day-to-day basis.

C. Criteria

1. A mid-concentration continuing calibration standard containing target compounds and surrogate compounds is analyzed at the beginning of each 12-hour analysis period following the analysis of the tune and prior to the analysis of the method blank and samples.

2. Method criteria state that a minimum daily RRF of 0.050 must be met for the SPCCs: 2,4-dinitrophenol, *N*-nitroso-di-*n*-propylamine, hexachlorocyclopentadiene, and 4-nitrophenol. However, determining data usability, any continuing calibration RRF must be greater than or equal 0.050.

3. Method criteria state that percent difference (percent drift) should be less than 20% for each CCC. Percent drift is calculated using the following equation:

$$\%Drift = ([C_I - C_c] / C_I) * 100$$

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where:

C_I = Calibration check compound standard concentration.
C_c = Measured concentration of continuing calibration CCC.

If the %Drift of each CCC is ≤20%, then the initial calibration is assumed to be valid. The CCCs are listed in the following table:

Base/Neutral Fraction	Acid Fraction
acenaphthene	4-chloro-3-methylphenol
1,4-dichlorobenzene	2,4-dichlorophenol
hexachlorobutadiene	2-nitrophenol
N-Nitrosodiphenylamine	phenol
di-*n*-octyl phthalate	pentachlorophenol
fluoranthene	2,4,6-trichlorophenol
benzo (a) pyrene	

It should be noted that if these CCCs are not target compounds for the specific analysis, then all target compounds are considered CCCs for the analysis.

If any SPCC RRF is <0.050 or CCC %Drift is >20%, the laboratory must correct the problem. If no source of the problem can be determined, the initial calibration sequence must be repeated.

It should be noted that the percent drift is equivalent to the percent difference between response factors as calculated according to CLP protocols.

Monitor the internal standard retention times and areas using the Form VIII-SV, or equivalent forms, for the following criteria:

- The retention time for any internal standard in the continuing calibration must be within 30 seconds of the internal standard retention times from the previous initial or continuing calibration.

- The internal standard area for any of the internal standards must be within -50% to +100% of the internal standard areas from the previous initial or continuing calibration.

- If these criteria are exceeded, the laboratory must inspect for malfunctions, and corrections must be made. When corrections are

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made, reanalysis of samples analyzed while the system was malfunctioning is required.

D. Evaluation

1. Verify that the continuing calibration was run at the required frequency and that the continuing calibration was compared to the correct initial calibration.

2. Evaluate the continuing calibration RRF for all semivolatile target compounds.

   a. Check and recalculate the RRF for at least one semivolatile target compound associated with each internal standard; verify that the recalculated value(s) agrees with the laboratory reported value(s). If errors are detected in the calculation of the RRFs, perform a more comprehensive recalculation.

   b. Verify that the RRF is ≥0.050 for all semivolatile compounds.

3. Evaluate the %Drift from the initial calibration for each continuing calibration.

   a. Check and recalculate the %Drift for at least one semivolatile target compound associated with each internal standard; verify that the recalculated value(s) agrees with the laboratory-reported value(s). If errors are detected in the calculation of the RRFs, perform a more comprehensive recalculation.

   b. Verify that the %Drift is ≤20% for all semivolatile compounds.

4. Verify that the continuing calibration internal standard area counts and retention times are acceptable when compared to the previous, initial, or continuing calibration internal standard responses.

E. Action

1. If any semivolatile target compound result has an RRF <0.50:

   a. Flag positive results for that compound as estimated (flagged "J").

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b. Flag "not-detects" for that compound with an "R".

2. If any semivolatile target compound has a %Drift >20%:

a. Flag positive results for that compound as estimated (flagged "J").

b. "Not-detects" for that compound may be qualified using professional judgment. In particular, if a high % Drift is due to a decrease in instrument sensitivity, qualify the associated "not-detected" results as estimated ("UJ"). If a high % Drift is due to an increase in instrument sensitivity, qualify the "not-detected" results as estimated ("UJ") and note in the QA review that, because of the increase in instrument sensitivity, the quantitation limit may be unacceptable as reported by the laboratory.

3. If a % Drift >90% is observed for a compound, qualify all positive results for the compound in the associated samples as estimated ("J") and all "not-detected" results in the associated samples as unreliable ("R"), whether or not the high % Drift is in the direction of increasing or decreasing sensitivity.

4. Data is not necessarily qualified if the continuing calibration standard does not display acceptable internal standard responses (in regard to area counts and retention times) when compared to the previous, initial, or continuing calibration standards. For instance, if a continuing calibration displayed poor area counts for one or more internal standards, but the associated samples displayed <u>acceptable</u> internal standard area counts when compared to the associated initial calibration, data should not be qualified because the sample quantitation is based on the average RRFs from the initial calibration. However, if the continuing calibration <u>and</u> associated samples display unacceptable internal standard responses, data for the samples should be qualified, even though the internal standard responses for the samples could be acceptable when compared to the associated continuing calibration. In any case, whenever a continuing calibration displays unacceptable internal standard area counts or retention times, consult the Project Manager or a senior chemist for guidance.

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VI. METHOD AND FIELD BLANK

A. Review Items

Blank Form I SV or equivalent, Form IV SV or equivalent, chromatograms, extraction logs, and quantitation reports.

B. Objective:

The assessment of blank analysis results is to determine the existence and magnitude of contamination problems. The criteria for the evaluation of blanks apply to any blank associated with the samples. If problems with any blank exist, all associated data must be carefully evaluated to determine whether or not there is an inherent variability in the data or if the problem is an isolated occurrence not affecting other data.

C. Criteria

1. No method-specific requirements concerning acceptable contaminant concentrations are listed in the method.

2. A method blank analysis must be performed each time a set of samples is extracted or whenever there is a change in reagents. A blank should be carried through all stages of sample preparation and analysis.

3. The frequency of field blanks is determined during the sampling event. A minimum of one field blank is suggested for each sample delivery group. Refer to the QAPP for project-specific criteria for the sampling frequency and acceptability of field blanks.

D. Evaluation

1. Review the results of all associated blanks on the forms and raw data (chromatograms and quantitation reports) to evaluate the presence of target and non-target compounds in the blanks. Tabulate the method blank and field results on the Environmental Standard Blank Analysis Results Forms. Convert method blank results reported in µg/l to µg/kg for qualification of soil samples.

2. Verify that a method blank analysis has been reported for each extraction batch.

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E. Action

If the appropriate blanks were not analyzed with the frequency described in Criteria 2 and 3 in Section VI.C, then the reviewer should use professional judgment to determine if the associated sample data should be qualified. If no field blanks are associated with the samples, a comment indicating that potential contamination due to field sampling can not be evaluated must be included in the QA review.

Action in the case of unusable blank results depends on the origin and circumstances of the blank.

Positive sample results are not qualified for associated blank contamination unless the concentration of the contaminant in the sample is ≤10× the amount in any blank for the common semivolatile laboratory contaminants (i.e., phthalates) or 5× the amount for other semivolatile target compounds. In instances where more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated method blank having the highest concentration for a contaminant. Qualification using multiple field blanks should be based upon comparison and association with the samples using the sample collection date. The project sample results must not be corrected by subtracting any blank value. When comparing blank concentrations to sample concentrations, the same weights, volumes, dilutions, and dry-weight correction factors must be considered when comparing blank results to project samples. It is often quicker and more convenient to compare instrument levels when considering blank contamination.

Specific actions are as follows:

1. If a semivolatile compound is found in a blank but not found in the sample, no action is taken.

2. If the sample result is greater than the quantitation limit (QL), but less than the required amount (5× or 10×) from the blank result, the sample results are qualified as not detected ("U").

3. If the sample result is positive, but less than the QL, and less than the required amount (5× or 10×) from the blank result, the result is raised to the QL and is flagged as not detected ("U").

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4. If the sample result is greater than the required amount (5× or 10×) from the blank result, the sample results are not qualified.

5. If gross contamination exists (i.e., saturated peaks by GC/MS), all affected compounds in the associated samples should be qualified as "R" due to interferences.

6. The same consideration given to the target compounds should also be given to tentatively identified compounds (TICs) that are found in both the sample and associated blank(s). However, the 5× and 10× rules do not apply and compounds found in both the blank and sample should be flagged "R" on the form I-TIC.

7. If low-level phthalates are not qualified based on blank contamination, a qualifier indicating phthalates are common laboratory contaminants should be included in the data validation report and urge caution when using the sample result.

VII. SURROGATE RECOVERY

A. Review Items

Form II SV, quantitation reports, and chromatograms

B. Objective

Laboratory performance on individual samples is established by means of spiking activities. The samples are spiked with surrogate compounds prior to sample purging. The evaluation of the results of these surrogate compounds is not necessarily straightforward. The sample matrix itself may interfere with the analysis due to such factors as high analyte concentration. Since the effects of the sample matrix are frequently outside the control of the laboratory and may present unique or unusual problems, the evaluation and review of data based on specific sample results is frequently subjective and demands analytical experience and professional judgment.

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C. Criteria

1. Surrogate compounds (three acid compounds and three base/neutral compounds) are added to all samples and blanks to measure their recovery in environmental samples and blank matrices.

At a minimum, the laboratory should update surrogate recovery limits on a matrix-by-matrix basis. Based on a minimum population of 20 samples, an average percent recovery and standard deviation of the percent recoveries are calculated by the laboratory. For each matrix, an upper and lower control limit for method performance for each surrogate standard is calculated using ± 3 times the calculated standard deviation. Once the laboratory-established limits are calculated, they are compared to the method specified control limits, as listed below. (The laboratory-established surrogate recovery limits must fall within the limits listed below.)

2. Recoveries for surrogate compounds in semivolatile samples and blanks must be within the limits specified below. If one or more surrogate recoveries in a sample are outside these limits, the laboratory must either reextract and reanalyze the sample, qualify all associated data as estimated.

Surrogate Compound Criteria

Surrogate	Water %R	Solid %R
nitrobenzene-d_5	35-114%	23-120%
2-fluorobiphenyl	43-116%	30-115%
terphenyl-d_{14}	33-141%	18-137%
phenol-d_6	10-94%	24-113%
2-fluorophenol	21-100%	25-121%
2,4,6-tribromophenol	10-123%	19-122%

D. Evaluation

1. Check raw data (i.e., chromatograms and quantitation reports) to verify the recoveries on the surrogate recovery Form II SV. Check for any calculation or transcription errors.

2. The following should be determined from the Surrogate Recovery Form(s):

a. If any surrogate compounds in the semivolatile fraction are out of specification, there should be a reanalysis to confirm that the

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noncompliance is due to sample matrix effects rather than laboratory deficiencies. However, Method 8270B does not require reanalysis of samples not meeting surrogate recovery criteria; the laboratory has the option of simply qualifying the data as "estimated concentration."

Note: When there are unacceptable surrogate compound recoveries followed by successful reanalyses, the laboratory may report only the results for the successful run.

b. Verify that no blanks have surrogate compounds outside the criteria.

E. Action:

Data are qualified based on surrogate compound results if the recovery of any semivolatile surrogate compound is out of specification. For surrogate compound recoveries out of specification, the following approaches are suggested:

1. If two or more surrogates in either semivolatile fraction (acid or base/neutral) have a recovery greater than the upper acceptance limit:

   a. Positive semivolatile target compounds for that fraction are qualified as estimated (flagged "J").

   b. Results for "not-detected" semivolatile target compounds for that fraction should not be qualified.

2. If two or more surrogates in either semivolatile fraction have a recovery [illegible]% but less than the lower acceptance limit:

   a. Positive semivolatile target compounds for that fraction are qualified as estimated (flagged "J").

   b. Results for "not-detected" semivolatile target compounds for that fraction should be qualified "UJ".

3. If any surrogate compound in either semivolatile fraction has a recovery less than 10%:

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a. Positive semivolatile target compounds for that fraction are qualified as estimated (flagged "J").

b. Results for "not-detected" semivolatile target compounds for that fraction should be qualified "R".

4. If a laboratory reports surrogate recovery ranges which are larger than those specified above, qualify sample data based on the recovery ranges and note the large recovery ranges in the QA review.

5. In the special case of a blank or laboratory control sample (LCS) with surrogates out of specification, the reviewer must give special consideration to the validity of associated sample data. Professional judgment should be used to determine if the surrogate outside criteria is an isolated occurrence or a systemic problem.

VIII. MATRIX SPIKE/MATRIX SPIKE DUPLICATES

A. Review Items

Form III SV or equivalent, chromatograms, and quantitation reports

B. Objective

Data for matrix spike/matrix spike duplicates are generated to determine long-term precision and accuracy of the analytical method on various matrices and demonstrate acceptable compound recovery by the laboratory at the time of sample analysis. These data alone are not used to evaluate the precision and accuracy for other samples.

C. Criteria

1. Matrix spike samples are analyzed at a frequency of one matrix spike per 20 samples of a similar matrix.

2. Many laboratories also perform a matrix spike duplicate analysis as an additional laboratory QC requirement, or as project-specific requirements at a frequency the same as for the matrix spike.

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3. Method 8270B provides three methods for determining the spike concentration. However, two of these methods require that the unspiked sample be analyzed prior to spiking and extracting the matrix spike sample. The analysis of the unspiked sample determines the background concentrations prior to spiking so appropriate spiking levels can be added to the matrix spike sample.

   As stated in the method, if it is impractical to determine background levels before spiking, the spike concentration should be at the regulatory concentration limit, or the larger of either 5× higher than the expected background concentration or 100 µg/l. For other matrices, the recommended spiking concentration is 20 times the EQL.

4. Environmental Standards interprets Method 8270B to indicate that the laboratory should perform a matrix spike analysis to include all target analytes. However, the method provides recovery limits for a specific number of compounds. Spike recoveries should be within the limits found in Table 6 of Method 8270B.

5. Laboratories may opt to perform a matrix spike/matrix spike duplicate analysis using a reduced list of analytes or the Contract Laboratory Spiking amounts and criteria. These criteria are provided below.

6. RPDs between matrix spike and matrix spike duplicate recoveries must be within the advisory limits provided on Form III VSV, as listed below:

MATRIX SPIKE/MATRIX SPIKE DUPLICATE CRITERIA

	Aqueous		*Solid*	
Compound	%R	RPD	%R	RPD
phenol	12-89%	42%	26-90%	35%
2-chlorophenol	27-123%	40%	25-102%	50%
1,4-dichlorobenzene	36-97%	28%	28-104%	27%
N-nitroso-di-*n*-propylamine	41-116%	38%	41-126%	38%
1,2,4-trichlorobenzene	39-98%	28%	38-107%	23%
4-chloro-3-methylphenol	23-97%	42%	26-103%	33%
acenaphthene	46-188%	31%	31-137%	19%
4-nitrophenol	10-80%	50%	11-114%	50%
2,4-dinitrotoluene	24-96%	38%	28-89%	47%
pentachlorophenol	9-103%	50%	17-109%	47%

	Aqueous		*Solid*	
Compound	%R	RPD	%R	RPD
pyrene	26-127%	31%	35-142%	36%

D. Evaluation

1. Verify that matrix spike or matrix spike/matrix spike duplicate samples were analyzed at the required frequency and that results are provided for each sample matrix.

2. Inspect results for the matrix spike or matrix spike/matrix spike duplicate recovery on Form III SV and verify that the results for recovery and RPD are within the limits on Table 6 in Method 8270D.

3. Verify transcriptions from raw data and verify calculations.

4. Compare %RSD results of nonspiked compounds between the unspiked result, matrix spike, and matrix spike duplicate samples.

E. Action

1. No action is taken on matrix spike or matrix spike/matrix spike duplicate data alone. However, using informed professional judgment, the data reviewer may use the matrix spike or matrix spike/matrix spike duplicate results in conjunction with the other QC criteria and determine the need for some qualification of the data.

2. Although the laboratory is required to use the matrix spike recovery ranges listed in Table 6 as method criteria, Environmental Standards will determine data usability using the following criteria. Note that data will not be qualified if the indigenous level of a compound in the unspiked sample is greater than 4× the spiking level for the compound.

   a. If any matrix spike compound has a recovery of <10%, positive results for that compound in the unspiked sample are qualified as estimated (flagged "J"), and "not-detected" results should be qualified "R".

   b. If any matrix spike compound has a recovery between 11% and 49%, positive results for that compound in the unspiked sample are

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qualified as estimated (flagged "J"), and "not-detected" results should be qualified "UJ".

c. If any matrix spike compound has a recovery between 50% and 135%, the results are acceptable and do not require qualification.

d. If any matrix spike compound has a recovery >135%, positive results for that compound in the unspiked sample are qualified as estimated (flagged "J").

3. If the laboratory performs an matrix spike/matrix spike duplicate analysis, qualify data based on the RPDs between the matrix spike and matrix spike duplicate concentrations in the following manner:

a. If the RPD for a compound exceeds 30% for an aqueous matrix spike/matrix spike duplicate analysis or 50% for a solid sample matrix spike/matrix spike duplicate analysis, flag the positive result for that compound in the unspiked sample as estimated ("J").

b. "Not-detected" results are not qualified due to high RPDs in the matrix spike/matrix spike duplicate analysis.

4. In the instance where the laboratory has adopted the Contract Laboratory Program (CLP) spiking list and acceptance criteria, note the issue in the QA review. In addition, data usability will be determined using the following criteria. As stated above, if the indigenous concentration of a compound in the unspiked sample is greater than 4× the spiking concentration, data will not be qualified based on the matrix spike/matrix spike duplicate recoveries for that compound.

a. If the recovery of a matrix spike compound in the semivolatile matrix spike and/or matrix spike duplicate has a recovery greater than the upper acceptance limit, positive results for that compound in the unspiked sample should be considered estimated (flagged "J").

b. If the recovery of a matrix spike compound in the semivolatile matrix spike and/or matrix spike duplicate has a recovery less than the lower acceptance limit and >10%, the positive result for that compound in the unspiked sample should be considered estimated (flagged "J"), and the "not-detected" result should be flagged "UJ"

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c. If the recovery of a matrix spike compound in the semivolatile matrix spike and/or matrix spike duplicate has a recovery less than 10%, "not-detected" results for that compound in the unspiked sample should be flagged "R".

d. If matrix spike/matrix spike duplicate pairs exceed the specified RPD, positive results for that compound in the unspiked sample should be considered estimated (flagged "J").

IX. BLANK SPIKES/LABORATORY CONTROL SAMPLES

A. Review Items

Form III or equivalent for LCS results, quantitation reports, and chromatograms

B. Objective

To establish the ability to generate acceptable accuracy and precision for each target analyte.

C. Criteria

1. If any analyte in the matrix spike sample fails the acceptance criteria for recovery, a QC reference sample (LCS) containing each analyte that failed the matrix spike recovery must be prepared and analyzed. If all target compounds meet acceptance criteria, an LCS is not required.

2. The frequency for the required analysis of the LCS is dependent upon the number of analytes analyzed, the complexity of the sample matrix, and laboratory performance. If a large number of analytes are analyzed, the probability that an LCS would be required is high. Therefore, many laboratories will prepare, extract, and analyze LCSs for all analytes with each SDG.

3. LCS recoveries should be within the limits provided in Table 6 of Method 8270B.

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D. Evaluation

1. Verify that LCS was analyzed for those analytes which displayed recoveries outside the specified recovery ranges for the matrix spike analyzed. Typically, LCS will contain all target analytes and, therefore, laboratory performance can be assessed for all analytes.

2. Inspect results for the LCS recoveries and verify that the results for the recoveries are within the limits on Table 6 in Method 8270B.

3. Verify transcriptions from raw data and verify correct calculations of LCS results.

E. Action

Although the laboratory is required to use the LCS recovery ranges listed in Table 6 as method criteria, Environmental Standards will determine data usability using the following criteria:

1. If any LCS compound has a recovery of <10%, positive results for that compound in all associated samples are qualified as estimated (flagged "J"), and "not-detected" results should be qualified "R".

2. If any LCS compound has a recovery between 11% and 49%, positive results for that compound in all associated samples are qualified as estimated (flagged "J"), and "not-detected" results should be qualified "UJ".

3. If any LCS compound has a recovery between 50% and 135%, the results are acceptable and do not require qualification.

4. If any LCS compound has a recovery >135%, positive results for that compound in all associated samples are qualified as estimated (flagged "J").

X. INTERNAL STANDARDS

A. Review Items

Form VIII SV or equivalent, quantitation reports, and chromatograms

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B. Objective

Internal Standards (IS) performance criteria ensure that GC/MS sensitivity and response are stable during every analysis.

C. Criteria

1. The recommended internal standards are 1,4-dichlorobenzene-d_4, naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12}, and perylene-d_{12}. The concentration of the internal standard in the extract should be 40 ng/µl for each internal standard.

2. Internal standard area counts from each sample, blank, or QC sample should not vary by more than a factor of two (-50% to +100%) from the associated calibration standard. It should be noted that this is <u>not</u> a requirement of the method.

3. Internal standard area counts from the continuing calibration must not vary by more than a factor of two (-50% to +100%) from the previous, initial, or continuing calibration.

4. The retention time of the internal standard from each sample, blank, or QC sample should not vary more than ±30 seconds from the associated calibration standard. It should be noted that this item is <u>not</u> a requirement of the method.

5. The retention time of the internal standards from the continuing calibration must not vary more than ±30 seconds from the previous, initial, or continuing calibration.

D. Evaluation

1. Check raw data (e.g., chromatograms and quantitation lists) to verify the internal standard retention times and areas reported on the Internal Standard Area Summary Forms (Form VIII SV).

2. Verify that all retention times and internal standard areas are within criteria.

3. If there are two analyses for a particular fraction, the reviewer must determine which are the best data to report. Considerations should include:

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a. Magnitu

b. Magnitu
shift.

c. Technica

d. Comparis
fraction.

e. Other QC

4. Verify stability of
criteria are not me
not a requirement

E. Action

1. If an internal standa
+100% of the area

a. Positive resu
qualified as e

b. "Not detecte
50% or gr
quantitation l

c. If extremely
exhibits a maj
indicated
qualified as u
response for
calibration star

2. If an internal standar
chromatographic profi
any false positives or n
reviewer may consider
fraction. If the mass s
need to be qualified as

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3. If one or more internal standards for a sample, blank, or QC sample displayed unacceptable retention times or area counts and the laboratory did not reanalyze the sample extract, include a comment concerning this issue in the QA review.

XI. TARGET COMPOUND IDENTIFICATION

A. Review Items

Form I SV or equivalent, quantitation report, mass spectra, and chromatograms

B. Objectives

The objective of the criteria for GC/MS qualitative analysis is to minimize the number of erroneous identifications of compounds. An erroneous identification can either be a false positive (reporting a compound present when it is not) or a false negative (not reporting a compound that is present).

C. Criteria

1. The relative retention times (RRTs) must be within ±0.06 RRT units of the standard RRT.

2. Mass spectra of the sample compound and a current laboratory-generated standard (i.e., the mass spectrum from the associated calibration standard) must match according to the following criteria:

   a. The characteristic ions from the reference mass spectrum (defined to be the three ions of greatest relative intensity or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum) must maximize in the same scan or within one scan of each other.

   b. The relative intensities of these characteristic ions must agree within ±30% between the standard and sample spectra. (Example: for an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 20% and 80%.)

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c. Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between the two isomer peaks is less than 25% of the sum of the two peak heights; otherwise, structural isomers are identified as isomeric pairs.

D. Evaluation

1. Check that the RRT of reported compounds is within ±0.06 RRT units of the standard RRT.

2. Check the sample compound spectra against the laboratory standard spectra to see that it meets the specified criteria.

3. The reviewer should be aware of situations (e.g., high concentration samples preceding low concentration samples) when sample carryover is a possibility and should use judgment to determine if instrument cross-contamination has affected any positive compound identification.

4. Check the chromatogram to verify that peaks are accounted for (i.e., major peaks are either identified as target compounds, TICs, surrogates, or internal standards). In addition, check for possible coeluting isomers (it is helpful to check the associated continuing calibration standard also).

E. Action

1. The application of qualitative criteria for GC/MS analysis of target compounds requires professional judgment. If it is determined that improper identifications were made, all such data should be qualified as "not detected" (flagged "U") or unusable (flagged "R"). A copy of the mass spectra must be placed in the support documentation section of the report to substantiate the qualifier.

2. Professional judgment must be used to qualify the data if it is determined that cross-contamination has occurred.

3. If structural isomers are observed to coelute on the GC column used for analysis, identify the coeluting isomers in the QA review. If practical to do so, change the data tables to reflect the fact that the isomers should be considered one analyte.

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XII. COMPOUND QUANTITATION AND REPORTED CRQLs

A. Review Items

Form I SV or equivalent, Case Narrative, quantitation reports, and chromatograms.

B. Objective

The objective is to ensure that reported quantitation results and contract required quantitation limits (CRQLs) are accurate.

C. Criteria

1. When a compound has been identified, the quantitation of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion.

2. If the %RSD of a compound's RRF is 15% or less, then the concentration in the extract may be determined using the average RRF from initial calibration date and the following equation:

$$C_{ex}(mg/L) = \frac{(A_x \times C_{is})}{(A_{is} \times \overline{RRF})}$$

where: C_{ex} - concentration of the compound in the extract

A_x - area of the quantitation ion of the compound of interest

A_{is} - area of the quantitation ion of the associated internal standard

C_{is} - concentration of the internal standard

$\overline{RRF}$ - average relative response factor from associated initial calibration

3. Alternatively, the regression line fitted to the initial calibration may be used for the determination of the extract concentration.

4. Compute the concentration of the analyte in the sample using the following equations:

a. The concentration of the analyte in the liquid phase of the sample is calculated using the concentration of the analyte in the extract and the volume of liquid extracted, as follows:

$$\text{Concentration in liquid } (\mu g / l) = \frac{(C_{ex} \times V_{ex}) \times D}{V_o}$$

where:

V_{ex} = extract volume, in ml
V_o = volume of liquid extracted, in l
D = dilution factor

b. The concentration of the analyte in the solid phase of the sample is calculated using the concentration of the pollutant in the extract and the weight of the solids, as follows:

$$\text{Concentration in solid } (\mu g / kg) = \frac{(C_{ex} \times V_{ex}) \times D}{W_s \times S}$$

where:

V_{ex} = extract volume, in ml
W_s = sample weight, in kg
S = percent solids of sample, expressed as a fractional number (e.g., 75% solids would be 0.75)
D = dilution factor

Note: Method 8270B does not specify dry-weight correction of results; however, this is normally done by the laboratory and is required in most QAPPs.

D. Evaluation

1. Verify that method quantitation limits reported by the laboratory are less than or equal to the CRQLs. If sample dilution is necessary due to elevated target compound concentrations, or if interference related to the sample matrix is observed, method quantitation limits reported by the laboratory may exceed required limits.

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2. For all fractions, raw data should be examined to verify the correct calculation of all sample results reported by the laboratory. Quantitation lists and chromatograms should be compared to the reported positive sample results and quantitation limits.

3. Verify that the correct internal standard, quantitation ion, and RRF are used to quantitate the compound. Verify that the same internal standard, quantitation ion, and RRF are used consistently throughout in both the calibration and the quantitation process.

4. Verify that the CRQLs have been adjusted to reflect all sample dilutions and dry-weight factors that are not accounted for by the method.

E. Action

If method quantitation limits reported by the laboratory exceed corresponding project-required quantitation limits and no sample dilutions were necessary, or matrix-related interferences observed, professional judgment should be used to assess the validity of the elevated sample results. The problem should be noted in the QA review.

If any discrepancies are found, the laboratory may be contacted by the designated representative to obtain additional information that could resolve any differences. If a discrepancy remains unsolved, the reviewer must use professional judgment to decide which value is the best value. Under these circumstances, the reviewer may determine if qualification of data is warranted.

XIII. TENTATIVELY-IDENTIFIED COMPOUNDS (if requested for analysis)

A. Review Items

Form I SV or equivalent, chromatograms, library search printouts, and spectra for the three TIC candidates

B. Objective

Chromatographic peaks in the semivolatile fraction that are not target analytes, surrogate compounds, or internal standard compounds are potential TICs. TICs must be qualitatively identified by a National Institute of Standards and Technology (NIST) mass spectral library search and the identifications must be assessed by the data reviewer.

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C. Criteria

For each sample, the laboratory must (if requested) conduct a mass spectral search of the NIST library and report the possible identity for the 20 to 30 largest semivolatile fraction peaks which are not surrogate compounds, internal standard compounds, or target compounds, but which have areas or heights greater than 10% of the area of height of the nearest internal standard. TIC results are reported for each sample on the Form I SV - TIC. Refer to the QAPP for specific requirements for TIC searches.

Note: CLP does not allow the laboratory to report any target compounds as TICs which are properly reported in another fraction. Most laboratories either follow this protocol for TICs or do not count these (as well as aldol condensates and laboratory artifacts) in the 20 to 30 TIC searches.

D. Evaluation

1. Guidelines for tentative identification are as follows:

a. Major ions (greater than 10% relative intensity) in the reference spectrum should be present in the sample spectrum.

b. The relative intensities of the major ions should agree within ±20% between the sample and the reference spectra.

c. Molecular ions present in the reference spectrum should be present in the sample spectrum.

d. Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination, interference, or coalition of additional TICs or target compounds.

e. When the above criteria are not met but in the technical judgment of the data reviewer or mass spectral interpretation specialist, the identification is correct, the data reviewer may report the identification.

f. In the data reviewer's judgment, if the identification is uncertain or there are extenuating factors affecting compound identifications, the TIC result may be reported as "unknown."

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2. Check the raw data to verify that the laboratory has generated a library search for all required peaks in the chromatograms for samples and blanks.

3. Blank chromatograms should be examined to verify that TIC peaks present in samples are not found in blanks. When a low-level, non-target compound that is a common artifact or laboratory contaminant is detected in a sample, a thorough check of blank chromatograms may require looking for peaks which are less than 10% of the internal standard height, but present in the blank chromatogram at a similar relative retention time.

4. All mass spectra for every sample and blank must be examined.

5. Since TIC library searches often yield several candidate compounds having a close matching score, all reasonable choices must be considered.

6. The reviewer should be aware of common laboratory artifacts/contaminants and their sources (e.g., aldol condensation products, solvent preservatives, and reagent contaminants). These may be present in blanks and not reported as sample TICs.

   a. Common laboratory contaminants: CO_2 (m/z 44), siloxanes (m/z 73), diethyl ether, hexane, certain freons (1,1,2-trichloro-1,2,2,-trifluoroethane, or fluorotrichloromethane), and phthalates at levels less than 100 µg/l or 4000 µg/kg.

   b. Solvent preservatives such as cyclohexene, which is a methylene chloride preservative, may be present. Related by-products include cyclohexanone, cyclohexenone, cyclohexanol, cyclohexenol, chlorocyclohexene, and chlorocyclohexanol.

   c. Aldol condensation reaction products of acetone include: 4-hydroxy-4-methyl-2-pentanone, 4-methyl-2-penten-2-one, and 5,5-dimethyl-2(5H)-furanone.

7. Occasionally, a target compound may be identified in the proper analytical fraction by non-target library search procedures, even though it was not found on the quantitation list. If the total area quantitation method was used, the reviewer should request that the laboratory recalculate the result using the proper quantitation ion. In addition, the reviewer should evaluate other sample chromatograms and check library reference retention times on

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quantitation lists to determine whether the false negative result is an isolated occurrence or whether additional data may be affected.

8. Target compounds could be identified in more than one fraction. Verify that quantitation is made from the proper fraction.

9. Library searches should not be performed on internal standards or surrogate compounds.

10. TIC concentration should be estimated assuming a RRF of 1.0 and quantitated from the internal standard nearest in retention time (free of interference) to the TIC.

E. Action

1. All TIC results identified with a specific compound name and Chemistry Abstracts Service (CAS) number should be qualified "NJ" (tentatively identified), with approximate sample concentrations. All other TICs (not identified as laboratory artifacts or blank contamination) should be flagged "J" as estimated concentrations.

2. General actions related to the review of TIC results are as follows:

   a. If it is determined that a tentative identification of a non-target compound is not acceptable, the tentative identification should be changed to "unknown" or an appropriate identification.

   b. If all contractually required peaks were not library searched and quantitated, the data reviewer should request these data from the laboratory.

3. When a compound is found in any blank, or is a suspected artifact or common laboratory contaminant, the result may be qualified as "R".

4. In deciding whether a library search result for a TIC represents a reasonable identification, professional judgment must be exercised. If there is more than one possible match, the result may be reported as "either compound X or compound Y." If there is a lack of isomer specificity, the TIC result may be changed to a non-specific isomer result (e.g., 1,3,5-trimethylbenzene may be changed to trimethylbenzene isomer) or to a compound class (e.g., 2-methyl-3-ethylbenzene to substituted aromatic compound).

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5. The reviewer may elect to report all similar compounds as a total (e.g., all alkanes may be summarized and reported as total hydrocarbons).

6. Other case factors may influence TIC judgments. If a TIC match is poor but other samples have a TIC with a good library match, similar relative retention time, and the same ions, identification information may be inferred from the other sample TIC results.

7. Physical constants, such as boiling point, may be factored into professional judgment of TIC results.

XIV. LABORATORY DUPLICATES

A. Review Items

Laboratory Duplicate Summary Form, chromatograms, and quantitation reports

B. Objective

Laboratory duplicate (or replicate, as stated in Method 8270B) samples are analyzed as an indication of overall laboratory precision. It is expected that soil duplicate results will have a greater variance than water matrices.

C. Criteria

1. The laboratory must analyze a duplicate (replicate) for each analytical batch to assess accuracy. For soil and waste samples where detectable amounts of organics are present, replicate samples may be appropriate in place of matrix spiked samples.

2. There are no specific method criteria established for laboratory duplicate comparability.

D. Evaluation

The reviewer should compare the results reported for each sample and duplicate and recalculate several of the relative percent differences (RPDs).

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E. Action

Positive results for a target compound should be flagged "J" in the sample and its duplicate if the following criteria are not met:

1. A control limit of ±20% (40% for solids) for the RPD shall be used for sample values greater than 5 × the QL.

2. A control limit of ± 1 the CRQL (±2 × the QL for solids) shall be used if at least one value is less than 5 × the QL.

If the laboratory did not perform an MSD or a laboratory duplicate analysis, include a deficiency to this effect in the quality assurance review.

XV. FIELD DUPLICATE

A. Review Items

Form I SVs, chromatograms, and quantitation reports

B. Objective

Field duplicate samples may be taken and analyzed as an indication of overall precision. These analyses measure both field and laboratory precision; therefore, the results may have more variability than laboratory duplicates which measure only laboratory performance. It is also expected that soil duplicate results will have greater variance than water matrices due to difficulties associated with collecting identical field samples. Refer to the QAPP for project-specific requirements for field duplicates.

C. Criteria

There are no specific method review criteria for field duplicate analyses comparability.

D. Evaluation

Samples which are field duplicates should be identified. The reviewer should compare the results reported for each sample and duplicate and calculate the

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relative percent difference (RPD) using Environmental Standards' computer generated forms.

E. Action

Positive results for a target compound should be flagged "J" in the sample and its duplicate if the following criteria are not met:

1. A control limit of ±40% (40% for solids) for the RPD shall be used for sample values greater than 5 × the QL.

2. A control limit of ± the CRQL or ±2 × the QL for solids shall be used if at least one value is less than 5 × the QL.

If a field duplicate pair was not submitted with the project samples, include a comment to this effect in the quality assurance review.

XVI. SYSTEM PERFORMANCE

A. Review Items

Form VIII SV, Form III SV, and chromatograms

B. Objective

During the period following instrument performance QC checks (e.g., blanks, tuning, etc.), calibration changes may occur in the system that degrade the quality of the data. While this degradation would not be directly shown by QC checks until the next required series of analytical QC runs, a thorough review of the ongoing data acquisition can yield indicators of instrument performance.

C. Criteria

There is no specific criteria for system performance. Professional judgment should be applied to assess the system performance.

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D. Evaluation

1. Abrupt, discrete shifts in the reconstructed ion chromatogram (RIC) baseline may indicate a change in the instrument's sensitivity or the zero setting. A baseline "shift" could indicate a decrease in sensitivity in the instrument or an increase in the instrument zero, possibly causing target compounds, at or near the detection limit, to miss detection. A baseline "rise" could indicate problems such as a change in the instrument zero, a leak or degradation of the column.

2. Poor chromatographic performance affects both qualitative and quantitative results. Indications of substandard performance include:

   a. High RIC background levels or shifts in absolute retention times of internal standards.

   b. Excessive baseline rise at elevated temperatures.

   c. Extraneous peaks.

   d. Loss of resolution.

   e. Peak tailing or peak splitting that may result in inaccurate quantitation.

E. Action

Professional judgment must be used to qualify the data if it is determined that system performance has degraded during sample analyses.

XVII. OVERALL ASSESSMENT OF DATA

A. Review Items

Entire data package, data review results and, if available, Quality Assurance Project Plan, and Sampling and Analysis Plan

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B. Objective

The overall assessment of a data package is a brief narrative in which the data reviewer expresses concerns and comments on the quality and, if possible, the usability of the data.

C. Criteria

Assess the overall quality of the data.

Review all available materials to assess the overall quality of the data, keeping in mind the additive nature of analytical problems.

D. Evaluation

1. Evaluate any technical problems which have not been previously addressed.

2. If appropriate information is available, the reviewer may assess the usability of the data to assist the data-user in avoiding inappropriate use of the data. Review all available information, including the Quality Assurance Project Plan, Sampling and Analysis Plan, and communication with the data-user that concerns the intended use and desired quality of these data.

E. Action

1. Use professional judgment to determine if there is any need to qualify data which were not qualified based on the QC previously discussed.

2. Write a brief narrative to give the user an indication of the analytical limitations of the data. If sufficient information on the intended use and required quality of the data are available, the reviewer should include his assessment of the usability of the data within the given context.

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XVIII. AUTHORITY

This data validation SOP for the analysis for semivolatile organic compounds by GC/MS has been prepared by Environmental Standards, Inc. This SOP represents internal control copy_____ issued to_____ and is not to be photocopied or used by any other entity except Environmental Standards, Inc. without expressed written permission.

SOP approved by:

_____ Date:_____
Rock J. Vitale, CPC
Technical Director of Chemistry/Principal

Control Copy No.:_____

Received by:_____

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STANDARD OPERATING PROCEDURE FOR VALIDATION OF TOTAL ORGANIC CARBON ANALYSES*

I. METHOD SUMMARY

The US EPA Methods 415.1 and 415.2 (Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020) and the SW-846 Method 9060 (Test Methods for Evaluating Solid Waste) examined in this standard operating procedure (SOP) are used to determine the concentration of total organic carbon (TOC) in aqueous samples. Generally, the organic carbon in a sample is converted to carbon dioxide (CO_2) and the CO_2 formed can be measured directly by an infrared detector (only for Methods 415.1 and 9060); alternatively, the organic carbon is converted to methane (CH_4) and measured by a flame ionization detector. The amount of CO_2 or CH_4 is directly proportional to the concentration of carbonaceous material in the sample. Carbonate and bicarbonate carbon represent an interference under the conditions of Methods 415.1 and 9060 and must be removed or accounted for in the final calculation. The homogenization of the samples in order to reduce the size of particulate matter may cause loss of purgeable organic carbon in Method 415.2.

II. TECHNICAL HOLDING TIMES

A. Review Items

Chain-of-Custody record, raw data, analytical result summaries, and Case Narrative

B. Objective

The objective is to ascertain the validity of results based on the holding time of the sample from the time of collection to time of analysis.

* See Section X for Authority and Application of this SOP.

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C. Criteria

The holding time for TOC samples is 28 days from the date of sample collection specified on the Chain-of-Custody records to sample analysis. If the project-specific quality assurance project plan (QAPP) requirements differ from those presented in the SOP, then technical requirements for sample holding times will be based on the project-specific QAPP. The samples must be preserved with hydrochloric acid (HCl only for Methods 415.1 and 9060) or sulfuric acid (H_2SO_4) to pH<2 and be kept cool (to 4 ± 2°C).

D. Evaluation

Verify that the samples were analyzed within 28 days of sample collection specified on the Chain-of-Custody records. Examine the sample records (if provided) to determine if samples were properly preserved.

E. Actions

If technical holding times are exceeded, sample preservation was not performed, or the temperature of the sample was greater than 6°C, document the deficiency in the quality assurance (QA) review and qualify the sample results according to the following criteria:

1. If holding times have been exceeded, qualify the positive results as estimated ("J") and qualify the "not-detected" results as "UJ".

2. If holding times have been grossly exceeded (sample analysis exceeds 2× the technical holding time), qualify the positive results as estimated ("J") and the "not-detected" results as unreliable ("R").

3. If indication of sample preservation was not provided on the Chain-of-Custody records, contact the field sampling team or the client for verification of correct sample preservation. If it can be documented that preservation was <u>not</u> performed, or if the pH of the samples upon receipt at the laboratory was not appropriate, flag all positive results as estimated ("J") and all "not-detected" results as "UJ".

4. If the temperature of samples upon receipt at the laboratory exceeds 6°C, attempt to ascertain how the temperature was obtained. If the temperature was obtained from a temperature bottle or by using an infrared (IR) gun, and the

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temperature is greater than 10°C, qualify positive results as estimated ("J") and "not-detected" results as "UJ".

III. INITIAL CALIBRATION

A. Review Items

Quality control (QC) summary forms and raw data

B. Objective

Compliance requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable quantitative and qualitative data. An initial calibration curve demonstrates that the instrument is capable of acceptable performance, with respect to sensitivity and linearity, at the beginning of the analysis, and continuing calibration verification documents that the initial calibration is still valid.

C. Criteria

The methods for total organic carbon analysis do not give any guidance on the generation of initial calibration curves for the analysis except that a series of standards should be used to prepare a calibration curve. Unless specified in the project-specific QAPP, the following will be used to assess the acceptability of the calibration curve:

1. The laboratory shall use a minimum of a four-point initial calibration sequence (a blank and three standards) for instrument standardization, unless otherwise specified in the method.

2. The correlation coefficient for the linear initial calibration curve shall be ≥0.995; if the correlation coefficient is less than 0.995, the laboratory shall prepare new standards, set up the instrument again, and recalibrate the instrument.

3. All positive results in the samples shall be reported from instrument levels which are within the calibration range of the instrument. If the instrument level for a sample exceeds the highest initial calibration standard concentration, the sample shall be diluted with reagent distilled water and reanalyzed.

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D. Evaluation

1. Verify that at least a four-point calibration was performed and that the correlation coefficient is at least 0.995.

2. Verify that all samples have an associated initial calibration.

3. Recalculate the correlation coefficient.

E. Action

1. If the correlation coefficient is < 0.995, qualify all positive results as estimated ("J").

2. Any discrepances/inconsistencies observed in the raw data from what the laboratory has reported must be resolved by the laboratory.

3. If a reported result is based on an instrument level which is greater than the calibration range of the instrument and the laboratory did not dilute and reanalyze the sample, include a statement to this fact in the QA review. In addition, qualify the positive results as estimated ("J").

IV. CONTINUING CALIBRATION

A. Review Items

QC summary forms and raw data

B. Objectives

The purpose of the continuing calibration analysis is to demonstrate acceptable instrument response throughout the period of time during which samples are analyzed. Instrument drift or analytical problems, which may have an adverse effect on the analytical results, are detected by poor results for the continuing calibration analyses.

C. Criteria

The methods for total organic carbon analysis do not clearly specify criteria for the frequency of continuing calibration analyses and the acceptable recoveries in the continuing calibration standards US EPA Method 415.2 requires the analysis of two

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"standards" at least once every day to check the linearity of the instrument. SW-846 Method 9060 requires the analysis of a "check" standard every 15 samples analyzed. Refer to the QAPP for project-specific requirements for continuing calibrations. For the purposes of data validation, the following criteria shall be used for assessing data quality:

1. The continuing calibration standard shall be analyzed at the beginning and end of the sample analysis and after every 15 sample analyses.

2. The continuing calibration standard shall display recoveries within the range of 85-115% or within the laboratory's acceptance criteria. Otherwise, the laboratory should restandardize the instrument, reverify the standardization (with the continuing calibration standard), and reanalyze all samples analyzed since the last compliant continuing calibration.

D. Evaluation

1. Review the raw data recordings and/or notebook pages to verify consistency between dates and times and consistency between raw data and QA summary forms.

2. Verify that continuing calibration standards were performed at a minimum of once after every 15 samples, before all samples are analyzed, and after the last sample is analyzed.

3. Verify that the percent recoveries were within 85-115% of the values obtained in the initial calibration or within the laboratory's acceptance criteria.

E. Action

1. Any inconsistencies/errors must be resolved by the laboratory. Analytical results should be considered tentative until the laboratory resolves these issues.

2. For continuing calibration outside the 85-115% criteria or outside the laboratory's acceptance criteria, positive results should be considered estimated and flagged "J".

Note: the continuing calibration standard should be applied to samples on both "sides" (before and after) until a compliant standard is obtained in both directions.

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3. If a continuing calibration analysis displays a recovery less than 85% or less than the laboratory's acceptance criteria, qualify the "not-detected" results as estimated ("UJ"). "Not-detected" results are not qualified if high recoveries are reported for the continuing calibration analyses.

4. If continuing calibration standards were not performed at the method or QAPP required frequency, note the deficiency in the QA review.

5. If a recovery outside the method or laboratory acceptance window is reported for a continuing calibration and the laboratory did not restandardize the instrument and reanalyze the associated samples, include a statement to this fact in the QA review.

V. METHOD BLANKS, CALIBRATION BLANKS AND/OR FIELD BLANKS

A. Review Items

1. Analytical results form, QC summary form, and raw data

B. Objective

Method blanks are distilled water blanks (initiated by the laboratory) carried through the sample preparation and analysis steps. Therefore, they monitor sample contamination which may occur during these steps in the laboratory. Calibration blanks are distilled water blanks that have not undergone any sample preparation steps. They monitor instrument drift which may result in false positive or false negative results for the samples. Field, equipment, and/or rinse blanks monitor the possible contamination of samples in the field (during the sampling event), during the shipment of the samples, during the preparation and analysis of the samples.

C. Criteria

SW-846 Method 9060 requires the analysis of one method blank with every batch of samples. The US EPA methods make references to reagent distilled water blanks. However, none of the total organic carbon methods give any guidance to the acceptable results for method blanks or calibration blanks. Refer to the QAPP for project-specific requirements for these QC analyses and for the frequency of collection of field, equipment, and/or rinse blanks and the acceptable results for these field QC blanks. For data validation purposes, the following criteria shall be used to assess the quality of the reported analytical results.

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1. A method blank shall be prepared with every batch of samples prepared for analysis or for every 20 samples, whichever is more frequent.

2. The continuing calibration blank shall be analyzed immediately after every continuing calibration standard.

3. The method blank; the continuing calibration blanks; and the field, equipment, and/or rinse blanks shall not display positive results greater than the reporting limit for the analysis.

4. The laboratory shall not perform blank subtraction when reporting results in the samples.

D. Evaluation

1. Verify the reported results against the raw data recordings and/or notebook pages to determine consistency and to determine if these blanks have acceptable calibrations.

2. Verify that every sample within the data set has an associated method blank and calibration blanks.

3. Verify that the method blank; the calibration blanks; and the field, equipment, and/or rinse blanks do not contain total organic carbon in excess of the reporting limit.

4. Verify that there is a field, equipment, and/or rinse blank for every data set of 20 samples or less (or per the requirement in the QAPP).

E. Actions

1. Any missing items, inconsistencies, or errors must be resolved by the laboratory. Until the laboratory clarifies/resubmits these items, the associated results are designated as tentative.

2. If the laboratory has utilized blank-subtraction, the laboratory must resubmit the data unsubtracted.

3. If a field, equipment, and/or rinse blank is not present, note this in the QA review.

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4. If the laboratory did not prepare and analyze a method blank, or analyze the continuing calibration blanks at the proper frequency, include a statement to this fact in the QA review.

5. The results of all laboratory blanks should be applied to all samples for data qualification purposes.

6. The results of the field blank should be applied to all samples collected on the same day.

7. In instances where more than one blank is associated with a given sample, qualification will be based upon a comparison with the associated blank having the highest concentration of a contaminant.

8. If TOC is present in any blank above the instrument detection limit or the reporting limit, the following apply:

   a. If a sample result is less than five times the concentration of total organic carbon in the blank, the sample result should be considered "not-detected" and qualified "U".

   b. If the sample result is greater than five times the blank result, no action will be taken.

   c. If TOC is detected in the blank but not in the samples, no action will be taken.

VI. MATRIX SPIKES/MATRIX SPIKE DUPLICATES AND LABORATORY CONTROL SAMPLES (LCSs)

A. Review Items

Analytical result forms, QC summary forms, and raw data

B. Objective

Data for matrix spikes (MS)/matrix spike duplicates (MSDs) are generated to determine long-term accuracy and precision of the analytical method on various matrices and to demonstrate acceptable compound recovery by the laboratory at the time of sample analysis. The data for laboratory control samples (LCSs) or blank spikes

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(BSs) are generated to determine analytical accuracy. The results of LCSs (BSs) are used to assess the accuracy of the entire sample batch.

C. Criteria

SW-846 Method 9060 requires the analysis of an MS sample for every 10 samples, but it does not specify criteria for acceptable recovery range for MS analysis or frequency and criteria for acceptable recovery range for LCS (BS) analysis. The US EPA methods do not specify criteria for the frequency of MS/MSD and LCS (BS) analysis or the acceptable recovery range. Refer to the QAPP for project-specific requirements concerning these QC analyses. For data validation purposes, the following criteria shall be used to assess data quality:

1. An MS/MSD and an LCS (BS) sample shall be prepared with every batch of samples prepared for analysis or for every 20 samples, whichever is more frequent.

2. The acceptable recovery range for the MS/MSD analyses will be the laboratory's QC limits, unless they are overly expanded, in which case, the acceptable recovery range will be 75-125%. Spike recovery limits do not apply when the sample concentration exceeds the spike concentration by more than a factor of four.

3. The laboratory's relative percent difference (RPD) QC limits will be used unless they are overly expanded, in which case, the maximum RPD between the results in the MS/MSD analysis will be 20%.

4. The acceptable recovery range for the LCS (BS) analyses will be the laboratory's QC limits, unless they are overly expanded, in which case, the acceptable recovery range will be 80-120%. If an unacceptable recovery is obtained for the LCS (BS) analysis, all associated samples shall be reprepared and reanalyzed.

5. The MS/MSD analysis will not be performed on a known field, equipment, or rinse blank.

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D. Evaluation

1. Verify that the MS/MSD and LCS (BS) samples were prepared and analyzed at the proper frequency.

2. Verify that there is consistency between the raw data and the recoveries reported.

3. Verify that the MS/MSD recoveries were within the laboratory's limits or within the range of 75-125%.

4. Verify that the LCS (BS) recoveries were within the laboratory's limits or within the range of 80-120%.

5. Verify that the MS/MSD analysis was not performed on a designated field, equipment, or rinse blank.

6. Verify that if the LCS (BS) analysis displayed an unacceptable recovery, the laboratory reprepared and reanalyzed associated samples.

E. Action

1. Any inconsistencies/errors must be resolved by the laboratory. Data are considered tentative until the laboratory resolves these issues.

2. If the MS/MSD was performed on a designated field, equipment, or rinse blank, note the deficiency in the quality assurance report.

3. If the recoveries for the MS/MSD are outside criteria, the following apply:

   a. If %R <75% or the lower limit reported by the laboratory but >30%, qualify positive results as estimated ("J") and "not-detected" results "UJ".

   b. If %R <30%, qualify positive results as estimated ("J") and "not-detected" results as unreliable ("R").

   c. If %R >125%, or the upper limit reported by the laboratory qualify positive results as estimated ("J"). The "not-detected" results do not require qualification.

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4. If the recoveries for the LCS (BS) are outside criteria, the following apply:

   a. If %R <80% or the lower limit reported by the laboratory but >40%, qualify positive results as estimated ("J") and "not-detected" results "UJ".

   b. If %R <40%, qualify positive results as estimated ("J") and "not-detected" results as unusable ("R").

   c. If %R >120% or the upper limit reported by the laboratory, qualify positive results as estimated ("J"). The "not-detected" results do not require qualification.

5. If the relative percent difference for the results from the MS/MSD analysis exceeds the laboratory limit or 20%, flag all positive results in the associated samples as estimated ("J"). Qualification of "not-detected" results in the samples is not necessary.

6. If the LCS (BS) analysis displays an unacceptable recovery and the laboratory did not reprepare and reanalyze the samples, note the deficiency in the quality assurance review.

VII. LABORATORY AND FIELD DUPLICATES

A. Review Items

Analytical results forms, QC summary forms, and raw data

B. Objectives

The laboratory duplicate analysis demonstrates the ability of the laboratory to achieve a certain level of precision in the procedures used for sample preparation and analysis. The field duplicate analysis provides an indication of overall (field and laboratory) precision and sample representativeness.

C. Criteria

The methods for total organic carbon do not specify criteria for the frequency of the laboratory duplicate analysis or the precision criteria required for the laboratory and field

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duplicate analyses results. Refer to the QAPP for project-specific requirements. For data validation purposes, the following criteria shall be used:

1. If an MS/MSD analysis is not performed, the laboratory shall prepare a laboratory duplicate sample with every batch of samples prepared for analysis or for every 20 samples, whichever is more frequent.

2. If both the initial and laboratory duplicate sample display results greater than 5× the method detection limit (MDL), then the RPD between the results shall not exceed the laboratory limits, unless they are overly expanded, in which case, the RPD between the results shall not exceed 20%.

3. If both the initial and field duplicate sample display results greater than 5× the MDL, then the RPD between the results shall not exceed 20%.

4. If one or both of the initial and/or laboratory/field duplicate samples display results less than 5× the MDL, then the difference between the two results shall not exceed ± MDL.

5. The laboratory duplicate analysis should be performed on a designated field, equipment, or rinse blank.

D. Evaluation

1. Verify that a laboratory duplicate was performed at a frequency of one per 20 samples or with every batch of samples prepared for analysis, whichever is more frequent.

2. Verify that there is consistency between the raw data and the RPDs reported.

3. Verify that the RPDs are within the laboratory's limits or less than 20% when both the initial and laboratory duplicate sample results are greater than 5× the MDL; otherwise, verify that the sample results are within the ± MDL.

4. Verify that the RPDs are less than 20% when both the initial and field duplicate sample results are greater than 5× the MDL; otherwise, verify that the sample results are within the ± MDL.

5. Verify that laboratory duplicates were not performed on field, equipment, or rinse blanks.

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E. Action

1. Any inconsistencies/errors must be resolved by the laboratory.

2. If the laboratory duplicate was not performed or not performed at the proper frequency, note the deficiency in the QA review.

3. If the laboratory duplicate was performed on a designated field equipment or rinse blank, note the deficiency in the QA review.

4. If the RPD are outside criteria, the following apply:

   a. If both the initial and laboratory duplicate analysis results are greater than 5× the MDL, and the RPD between the results is greater than the laboratory's control limit, flag all positive results in the associated samples as estimated ("J"). Qualification of "not-detected" results is not required.

   b. If both the initial and field duplicate analysis results are greater than 5× the MDL and the RPD between the results is greater than 20%, flag all positive results in the associated samples as estimated ("J"). Qualification of "not-detected" results is not required.

   c. If one or both of the initial and/or laboratory or field duplicate sample results is less than 5× the MDL and the difference between the results is greater than the ± MDL, flag all positive results in the associated samples as estimated ("J"). Qualification of "not-detected" results is not required.

VIII. SAMPLE RESULT VERIFICATION

A. Review Items

Analytical results forms and raw data

B. Objective

The objective is to ensure that reported quantitative results and reported quantitation limits (QLs) are accurate and that all reported positive results were calculated within the calibration range of the instrument.

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C. Criteria

The laboratory shall provide all raw data necessary to recalculate all positive results, and to verify the reported "not-detected" results from the raw data. SW-846 Method 9060 requires quadruplicate analysis of the samples. Both the average value and the range must be reported.

D. Evaluation

1. Verify that all required data is present. Verify that all laboratory calculations are present for positive sample results and QC sample results.

2. Recalculate and confirm the positive sample results.

3. Verify that all positive results are quantitated within the calibrated range.

4. Verify that quadruplicate analysis of the samples was performed if Method 9060 was used and the average value and the range were reported.

E. Action

If there are any discrepancies found, the laboratory may be contacted to obtain additional information that could resolve differences. If a discrepancy remains unresolved, the reviewer may determine that qualification of the data is warranted.

1. Any data found incorrect and/or missing (i.e., sample calculations) must be resolved and submitted by the laboratory.

2. Reported positive results quantitated beyond the calibrated range should be estimated and flagged "J".

3. If the method requirements for sample analysis were not followed, note the deficiency in the quality assurance review.

IX. OVERALL ASSESSMENT OF DATA

A. Review Items

Entire data package, data review results, the QAPP, and Sampling and Analysis Plan

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B. Objective

The overall assessment of a data package is a quality assurance review in which the data reviewer expresses concerns and comments on the quality and the usability of the data.

C. Criteria

Assess the overall quality of the data.

Review all available materials to assess the overall quality of the data keeping in mind the additive nature of analytical problems.

D. Evaluation

1. Evaluate any technical problems which have not been previously addressed.

2. If appropriate information is available, the reviewer may assess the usability of the data to assist the data user in avoiding inappropriate use of the data. Review all available information, including the QAPP and Sampling and Analysis Plan, and communicate with the client any concerns relating to the intended use and desired quality of these data.

E. Action

1. Use professional judgment to determine if there is any need to qualify data which were not qualified based on the QC previously discussed.

2. Write a fully documented QA review which provides the client with an [illegible] of the analytical limitations of the data. If sufficient information on the intended use and required quality of the data are available, the reviewer should include his assessment of the usability of the data within the given context.

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X. AUTHORITY

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STANDARD OPERATING PROCEDURES FOR DATA VALIDATION OF NONHALOGENATED VOLATILE ORGANICS BY SW-846 METHOD 8015A*

I. METHOD SUMMARY

Method 8015A provides gas chromatographic (GC) conditions for the detection of nonhalogenated volatile organic compounds (VOCs). Samples may be introduced into the GC using direct injection or purge and trap (Method 5030). The main types of interference are contamination from high level samples that are shipped or stored with the samples, instrument carry-over, and contaminated reagents.

SW-846 methods allow for considerable amount of laboratory interpretation in regard to the analytical requirements and data interpretation. Therefore, separate laboratories may perform the same method and utilize different acceptance criteria and different result interpretations. In addition, a project specific quality assurance project plan (QAPP) might include requirements which differ from those presented in the standard operating procedure (SOP). Therefore, some of the sections in the SOP might not be applicable to all situations.

II. TECHNICAL HOLDING TIMES

A. Review Items

Analytical results, Chain-of-Custody records, raw data, and Case Narrative

B. Objective

The objective is to ascertain the validity of results based on the holding time of the sample from the time of collection to the time of analysis.

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* **See Section XIV for Authority and Application of this SOP.**

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C. Criteria

Technical requirements for sample holding times are based on SW-846 Chapter 4, Table 4-1 or the project-specific QAPP. The holding time criterion for VOCs in cooled (4±2°C) solid samples and in cooled (4±2°C) and chemically preserved (pH<2 with HCl) water samples is 14 days from collection to analysis. For unpreserved aqueous samples, the holding times are 14 days from collection to analysis for non-aromatic compounds and 7 days from collection to analysis for aromatic compounds. It should be noted that Region II specifies the holding time for cooled (4±2°C) solid samples is 10 days from collection to analysis.

D. Evaluation

Technical holding times are established by comparing sampling dates on the Chain-of-Custody records to the dates of analysis on the sample analysis summary and raw data. Examine the sample records to determine if samples were preserved (cooled [4±2°C] and pH<2).

E. Evaluation

If technical holding times are exceeded, document in the quality assurance (QA) review that holding times were exceeded and qualify the sample results according to the following criteria:

1. If correctly chemically preserved samples were analyzed between 15 and 28 days from collection, flag positive results as estimated ("J"). The quantitation limit for the compounds in the sample may be higher than reported. Flag the "not-detected" results "UJ". For Region II, if solid samples were analyzed between 11 and 20 days from collection, flag positive results as estimated ("J") and the "not-detected" results "UJ".

   If non-chemically preserved (pH>2) aqueous samples were analyzed between 8 and 14 days from collection, flag positive results for aromatic compounds as estimated ("J") and the "not-detected" results for aromatic compounds "UJ". Non-aromatic compounds are qualified as per Sections E.1 and E.3, regardless of chemical preservation.

3. If correctly preserved samples were analyzed more than 28 days from collection, flag positive results as estimated ("J") and the "not-detected" results "R". For Region II, if solid samples were analyzed more than 20

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days from collection, flag positive results as estimated ("J") and the "not-detected" results "R".

4. If non-chemically preserved (pH<2) aqueous samples were analyzed more than 14 days from collection, flag positive results for aromatic compounds as estimated ("J") and the "not-detected" results for aromatic compounds "R". Non-aromatics are qualified as per Sections E.1 and E.2 above, regardless of chemical preservation.

5. If a sample is received at the laboratory with a temperature greater than 6°C but less than or equal to 10°C and the temperature of the cooler was measured with an infrared (IR) gun or with a temperature bottle, flag positive results for all compounds as estimated ("J") and all "not-detected" results "UJ". In addition, note the deficiency in the QA report.

6. If a sample is received at the laboratory with a temperature greater than 10°C and the temperature of the sample cooler was measured with an IR gun or with a temperature bottle, flag all positive results as estimated ("J") and all "not-detected" results as unusable ("R"). In addition, note the deficiency in the QA report.

7. If high temperatures were noted for project samples, but the laboratory used a method other than temperature bottles or IR guns for measuring the cooler temperatures, comment in the report that high sample temperatures were noted but that the method of measuring the cooler temperature may not reflect actual sample temperatures, and data was not qualified based on this issue. In addition, note if the laboratory indicated the presence of wet ice or "blue ice" in the sample cooler.

III. INITIAL CALIBRATION

A. Review Items

Analytical sequences, calibration summary forms, integration reports, and chromatograms

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B. Objective

Compliance requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable qualitative and quantitative data for non-halogenated VOCs.

C. Criteria

1. Initial calibration standards containing the volatile organic target compounds are analyzed at five concentrations (over the linear range) at the beginning of each analytical sequence, or as necessary if the continuing calibration acceptance criteria are not met.

2. The low standard (at or slightly above the method detection limit [MDL]) must be visible on the chromatogram.

3. If the percent relative standard deviation (RSD) of the calibration factors (CFs) of the initial calibration standards is less than or equal to 20%, linearity through the origin can be assumed, and the average calibration factor can be used in place of a calibration curve. If the RSD is in excess of 20%, then a calibration curve (polynomial, cubic, etc.) must be used.

4. If Method 5030 is used, all of the analyses must be performed with a purge temperature of [illegible].

D. Evaluation

1. Verify that the concentrations of the standards used for the initial calibration were based on the laboratory analytical SOP and raw data.

2. Verify that the correct initial calibration was used for all samples.

3. If Method 5030 was used, verify that a heated purge was used.

4. Verify that the sample results were calculated correctly. Specifically, if the RSD is ≤20%, the average CF from the initial calibration should be used. If the RSD >20%, the entire curve representing the initial calibration standards must be used.

5. Evaluate the initial calibration CFs for all target compounds.

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a. Check and recalculate the CFs and average CF for at least three target compounds; verify that the recalculated value(s) agrees with the laboratory-reported value(s). If errors are detected in the calibrations, perform a more comprehensive recalculation.

b. Verify that the low calibration standard is clearly visible on the chromatogram.

6. Evaluate the RSD for all target compounds.

a. Check and recalculate the RSD for one or more target compounds); verify that the recalculated value(s) agrees with the laboratory-reported value(s). If errors are detected in the calculations, perform a more comprehensive recalculation.

b. Verify that all target compounds have an RSD less than or equal to 20% if the average CF is used for quantitation.

c. Visually verify that the calibration curve is an acceptable curve. Consult with a senior QA chemist if necessary.

B. Action

1. If any target compound result is associated with a low concentration initial standard that is not visible on the chromatogram, professional judgment must be used to determine the magnitude of the bias (depends on the concentration of the low standard relative to the reporting limit).

Flag "not-detected" results for that compound with a "UJ". If the [illegible] indicate a severe lack of sensitivity (e.g., the higher calibration standards are barely visible), the reviewer may elect to flag "not-detected" results for that compound with an "R"

2. If the initial calibration standards and the associated samples were not performed similarly (i.e., the initial calibration standards were heated and the samples were not heated), flag "not-detected" results for all compounds with a "UJ" and the reported positive results with a "J".

3. If any target compound has an RSD greater than 20% but less than 50% and the average CF was used for quantitation:

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a. Flag positive results for that compound as estimated ("J").

b. "Not-detected" results would not be qualified.

4. If any target compound has an RSD greater than 50% but less than 90% and the average CF was used for quantitation:

a. Flag positive results for that compound as estimated ("J").

b. Flag "not-detected" results "UJ".

5. If any target compound has an RSD greater than 90% and the average CF was used for quantitation:

a. Flag positive results for that compound as estimated ("J").

b. Flag "not-detected" results "R".

6. If a calibration curve was used for quantitation, professional judgment will be used to determine the appropriateness of the curve generated. For instance, the data reviewer will determine if the average percent error for the calibration standards is acceptable, with special attention to quantification at the QL.

V. CONTINUING CALIBRATIONS

A. Review Items

Analytical sequences, calibration summary forms, integration reports, and chromatograms

B. Objective

Continuing calibrations are performed to verify that the initial calibration curve is still acceptable for quantitation of results with respect to sensitivity and accuracy on a day-to-day basis.

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C. Criteria

1. Continuing calibration standards containing target compounds and surrogate compounds are analyzed at a minimum of every working day, or at the frequency indicated in the project specific QAPP.

2. The concentration of the continuing calibration check will be around the midpoint of the calibration curve.

3. If Method 5030 is used, the continuing calibration check must be performed with a heated purge.

4. The percent difference (%D) between the projected concentration and the obtained concentration must not differ by more than the acceptance criteria of 15% or the laboratory-defined acceptance limits. If the difference is outside of the acceptance limit, the continuing calibration standard may be reinjected once. If the criterion is still not met, a new initial calibration must be performed.

5. All succeeding continuing calibrations after the first continuing calibration standard has been used to establish daily retention time (RT) windows, must be within the established RT windows.

D. Evaluation

1. Verify that the continuing calibration was run at the required frequency and that the continuing calibration was compared to the correct initial calibration.

2. If Method 5030 was used, verify that a heated purge was used.

3. Evaluate the continuing calibration %D for all target compounds:

a. Quantitatively verify that the recovery was calculated properly for at least three target compounds; verify that the recalculated value(s) agrees with the laboratory-reported value(s). If errors are detected in the calculation of the recovery, perform a more comprehensive recalculation.

b. Verify that the peaks for the continuing calibrations are clearly visible on the chromatograms.

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4. Verify that the %D is within the acceptance limits for all target compounds.

5. Verify that after the daily RT windows have been established, all target analytes in the subsequent calibration checks are within the established RT windows.

E. Action

1. If continuing calibrations were not performed at the specified frequency, this should be indicated in the QA review.

2. If the continuing calibration standards and the samples associated were not performed similarly (i.e. the continuing calibration standards were heated and the samples were not heated), flag "not-detected" results for all compounds with a "UJ" and reported positive results with a "J".

3. If any target compound has a %D greater than 15% in the continuing calibration standard with increased instrument sensitivity:

   a. Flag positive results for that compound as estimated ("J").

   b. Compound quantitation limits would not be qualified.

4. If any target compound has a %D greater than 15% but less than 70% in the continuing calibration standard with decreased instrument sensitivity:

   a. Flag positive results for that compound as estimated ("J").

   b. Flag "not-detected" results for that compound "UJ".

5. If any target compound has a %D greater than 70% in the continuing calibration standard with decreased instrument sensitivity:

   a. Flag positive results for that compound as estimated ("J").

   b. Flag "not-detected" results for that compound "R".

6. If any target compound is outside the daily established RT windows, the associated sample chromatograms must be carefully evaluated using reviewer-generated expanded RT windows.

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a. If the chromatograms reveal the absence of peaks possibly corresponding to the target compounds of interest using expanded RT windows, data usability is not affected. A notation should be included in the QA review.

b. If the chromatograms reveal peaks corresponding to the target compound of interest using expanded RT windows, "not detected", as well as reported positive sample results for the compound outside the RT window, should be flagged "R".

7. If target analyte peaks in the controlling calibration are not visibly present on the chromatograms, "not detected" sample results for those analytes should be flagged "R".

V. BLANKS

A. Review Items

QC summary forms, chromatograms and integration reports

B. Objective

The assessment of blank analysis results determines the existence and magnitude of contamination problems. The criteria for evaluation of blanks apply to any type of blank associated with the samples. If problems with any blank exist, all associated data must be carefully evaluated to determine whether or not there is an inherent variability in the data or if the problem is an isolated occurrence not affecting the other data.

C. Criteria

1. No contaminants should be found in the blank at or above the reporting limits. If the laboratory method blank has target analytes at or above the reporting limit, the entire sample batch is reanalyzed.

2. A method blank analysis must be performed at least once for each batch of ≤20 samples of a similar matrix. Refer to the QAPP for project-specific criteria for trip blanks, field blanks, equipment blanks, and rinse blanks.

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3. The method blank must be analyzed daily and must be reported for each instrument used for sample analysis.

4. If Method 5030 is used, the method blank must be performed with a heated purge.

D. Evaluation

1. Review the results of all associated blanks on the forms and raw data (chromatograms and integration reports) to evaluate the presence of target compounds in the blanks.

2. Verify that a method blank analysis has been reported for each day and on each instrument used to analyze samples.

3. If Method 5030 was used, verify that a heated purge was used.

E. Action

If the appropriate blanks were not analyzed with the frequency described in Criteria 2 and 3 in Section VIII, then the reviewer should use professional judgment to determine if the associated sample data should be qualified.

Action in the case of unsuitable blank results depends on the origin and circumstances of the blank.

Positive sample results are not qualified for associated blank contamination unless the concentration of the compound in the sample is less than or equal to 5× the amount found in the blank for that target compound (10× for the ketones). In instances where more than one blank is associated with a given sample, qualification should be based upon a comparison with the associated blank having the highest concentration for a contaminant. The results must not be corrected by subtracting any blank value.

Specific actions are as follows:

1. If a target compound is found in the blank but not in the sample, no action is taken.

2. If the sample result is greater than the quantitation limit (QL) but less than the required amount (5× from the blank result or 10× for the ketones), the sample results are qualified as "not-detected" ("U").

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3. If the sample result is positive but less than the QL and less than the required amount (5× from the blank result or 10× for the ketones), the result is raised to the QL and is flagged as "not detected" ("U").

4. If the sample result is greater than the required amount (5× from the blank result or 10× for the ketones), the sample results are not qualified.

5. If gross blank contamination exists (i.e., saturated peaks on the GC), all affected compounds (compounds which would be expected to elute during the observed interference) in the associated samples should be qualified as "R" due to interference.

VI. SURROGATE RECOVERY

A. Review Items

QC Summary forms, integration reports, and chromatograms

B. Objective

Laboratory performance (accuracy) on individual samples and blanks is established by means of spiking activities. All samples and blanks are spiked with the surrogate compound(s) prior to sample analysis.

C. Criteria

Recoveries for the surrogate(s) should be within the limits specified by the laboratory for all samples, or the sample must be reanalyzed. Recoveries outside criteria due to dilutions of the samples are acceptable.

D. Evaluation

1. Check raw data (i.e., chromatograms and integration reports) to verify the recoveries on the surrogate recovery QC summary form. Check for any calculation or transcription errors.

2. The following should be determined from the surrogate recovery QC summary form.

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a. If any surrogate compound is below the acceptance criterion, there should be a reanalysis to confirm that the noncompliance is due to sample matrix effects rather than laboratory deficiencies.

Note: When there is an unacceptable surrogate compound recovery following successful reanalysis, the laboratory is required to report only the results for the successful analysis.

b. The laboratory failed to perform appropriately if a surrogate recovery is below the acceptance limit with no evidence of reanalysis. Be certain that the laboratory is utilizing the criterion for reanalysis.

c. Verify that no blanks have surrogate recoveries outside the acceptance criteria.

E. Action

Data are qualified based on surrogate compound results if the recovery for the surrogate compound is out of specification. For surrogate compound recoveries out of specification, the following approaches are suggested (Note: if the laboratory-supplied surrogate recovery limits are unreasonably wide, ask the Project Manager for clarification of usability limits for the surrogate recoveries.):

1. If the surrogate recovery is greater that the upper acceptance limit:

a. Positive results for target compounds are qualified as estimated ("J").

b. Results for "not-detected" target compounds should not be qualified.

2. If the surrogate recovery is greater than or equal to 10% but less than the lower acceptance limit:

a. Positive target compounds are qualified as estimated ("J").

b. Results for "not-detected" compounds should be qualified "UJ".

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3. If the surrogate recovery is less than 10%:

   a. Positive target compounds are qualified as estimated ("J").

   b. Results for "not-detected" compounds should be qualified "R".

VII. INTERNAL STANDARDS (if used)

A. Review Items

QC summary forms, integration reports, and chromatograms

B. Objective

Internal standards performance ensures that GC sensitivity and response are stable during each analysis.

C. Criteria

1. Internal standard compounds are added to all samples and blanks to ensure that sensitivity and response are stable during each analysis.

2. Criteria for internal standards are typically specified in the QAPP or by the laboratory. If criteria are not specified, utilize the following for guidance:

RTs of the internal standards must not vary more than ±30 seconds from the RTs of the associated calibration standard, and area counts of the internal standards must not vary more than a factor of two (-50% to +100%) from the associated calibration standard for all samples.

D. Evaluation

1. Verify that internal standard compounds were added to all samples and blanks.

2. If any internal standard compound is outside the acceptance criteria (laboratory-specified), there should be a reanalysis to confirm that the noncompliance is due to sample matrix effects rather than laboratory deficiencies.

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E. Action

Data are qualified if internal standard compound results are out of specification. For internal standard compounds out of specification, the following approaches are suggested:

1. If an internal standard area count for a sample is greater than the upper acceptance limit, flag positive results "J" and "not-detected" results "UJ" for the compounds quantitated from the internal standard.

2. If an internal standard area count is less than the lower acceptance limit but greater than or equal to 25% of the associated calibration internal standard, flag positive results "J" and "not detected" results "UJ" for the compounds quantitated from the internal standard.

3. If an internal standard area count is less than 25% of the associated calibration internal standard, flag positive results "J" and "not-detected" results "R" for the compounds quantitated from the internal standard.

4. When the internal standard RT varies by more than 30 seconds and no peaks are observed in the sample chromatogram, then there may be no impact on data usability. However, if peaks are observed in the sample chromatogram, professional judgment will be exercised on a case-by-case basis.

VIII. MATRIX SPIKES/MATRIX SPIKE DUPLICATES/BLANK SPIKES (OR LCS)

A. Review Items

QC summary forms, chromatograms, and integration reports

B. Objective

Data for matrix spikes/matrix spike duplicates (MS/MSDs) are generated to determine long-term accuracy and precision of the analytical method on various matrices and to demonstrate acceptable compound recovery by the laboratory at the time of sample analysis. These data alone are not used to evaluate the accuracy of other samples. The data for blank spikes (BSs) or laboratory control samples (LCSs) are generated to determine analytical accuracy. The results of BSs are used to assess the accuracy of the entire sample batch.

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C. Criteria

1. MS/MSD samples are analyzed at a frequency of one per 20 samples. BS (or LCS) samples may also be analyzed at a frequency of one per 20 samples.

2. MS/MSD/BS (or LCS) recoveries and RPDs for MS/MSDs should be within the laboratory-specified or QAPP-specified acceptance criteria.

3. If any recovery is below the acceptance criteria (laboratory-generated only) in the BS (or LCS), all of the associated samples must be reanalyzed.

D. Evaluation

1. Verify that an MS/MSD and BS (or LCS) were analyzed at the required frequency.

2. Inspect results for the MS/MSD/BS (or LCS) recoveries and MS/MSD relative percent differences (RPDs) on the quality control (QC) summary forms and verify that the results for the recoveries are within the specified limits.

3. Verify transcriptions from raw data and verify calculations.

4. Compare RPD results of nonspiked compounds between the unspiked result and the MS/MSD results.

E. Action

1. In instances where the MS/MSD results are outside acceptance criteria, the following criteria should be used for the qualification of the sample that was spiked:

a. If an MS compound in the MS/MSD has a recovery greater than the upper acceptance limit, positive results for that compound in the unspiked sample should be considered estimated ("J"), and the "not-detected" results are not qualified.

b. If an MS compound in the MS/MSD has a recovery less than the lower acceptance limit and > 10%, the positive result for that

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compound in the unspiked sample should be considered estimated ("J"), or the "not-detected" result should be flagged "UJ".

c. If an MS compound in the MS/MSD has a recovery < 10%, the positive result for that compound in the unspiked sample should be considered estimated ("J"), or the "not-detected" result should be flagged "R".

d. If the RPD is outside the acceptance criteria, the positive results for that compound in the unspiked sample should be considered estimated ("J").

2. In instances where the LS (or LCS) recoveries are outside acceptance criteria (Actions 1a, 1b, and 1c above) are applied to all samples (of a similar matrix) in the batch. In addition, if the laboratory performs a LS/BSD or LCS/LCSD analysis, evaluate the RPDs for the analysis as per the MS/MSD analysis and qualify all associated sample results for high RPDs.

3. If the RSD between results for unspiked compounds in the MS/MSD exceeds 20% for aqueous samples (40% for solid samples) and all results in the MS/MSD and unspiked sample are greater than 5× the reporting limit, flag the positive results in the unspiked sample as estimated ("J").

4. If the range of results for unspiked compounds among the MS/MSD and unspiked aqueous sample exceeds the CRQL (2×CRQL for solid samples) and at least one of the results is less than 5× the CRQL, flag the positive result for the unspiked compounds as estimated ("J").

IX. TARGET COMPOUND IDENTIFICATION

A. Review Items

QC summary forms, Case Narratives, integration reports, and chromatograms

B. Objective

The objective is to ensure that the compound identifications are accurate based on RT windows, peak resolution, and the linear range of the system.

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C. Criteria

1. RT windows must be established to ensure the GC system is within optimum operating conditions. Ideally, the laboratory makes three injections of all single component standard mixtures throughout the course of a 72-hour period. Serial injections over less than a 72-hour period result in RT windows that are too tight. The laboratory then calculates the standard deviation of the three RTs (use any function of RT, including absolute RT or relative RT) for each single component standard.

2. Daily RT windows should be established for each compound. The RT for each compound mentioned above is used as the midpoint of the window for that day. The daily RT window equals the midpoint ± 3 times the standard deviation determined above.

3. Tentative identification of a compound occurs when a peak from a sample extract falls within the daily RT window. Normally, confirmation is required on a second GC column. Confirmation may not be necessary if the composition of the sample matrix is well established by prior analyses.

4. If the target compound peak responses exceed the linear range of the calibration curve, the extract should be diluted and reanalyzed. All peaks should be on scale. Overlapping peaks are not always evident when peaks are off scale. Computer reproduction of chromatograms, manipulated to ensure all peaks are on scale over a 100-fold range, are acceptable if linearity is demonstrated. Peak height measurements are recommended over peak area integration when overlapping peaks cause errors in area integration. If peak detection is prevented by the presence of interferences, further cleanup is required.

D. Evaluation

1. Second-column confirmation should be provided; if it was not, attempt to obtain the confirmation analysis from the laboratory. If the confirmation analysis cannot be provided or was not performed, write a comment in the QA review.

2. Verify that the target compound peaks have unique RT windows by viewing the initial calibration standards or any RT window summary information that the laboratory may have provided.

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3. Verify that for any target compound responses exceeding the linear range of the calibration curve, the extracts were diluted and reanalyzed for those particular compounds.

4. Study the chromatograms for unstable baselines, coeluting peaks, poor resolution, matrix interferences, or any other problems that would hinder the identification of target compounds (producing false negatives or false positives).

E. Action

1. If a laboratory reports a positive result for a compound which displays a RT outside the specified RT window, check the surrogate compound (if used) for a shift in RT. If a similar shift is observed with the surrogate compound, the identification may be acceptable. Check with the Project Manager and include a comment in the QA review concerning this issue.

2. If, in the situation stated above, the surrogate does not display a RT shift, then delete the positive result from the data tables or Form I and include a statement in the report.

3. If the laboratory did not report a positive result for a compound (peaks within the RT windows for both columns, if a confirmation column is used) and the result is greater than the reporting limit (or quantitation limit), add the result to the data tables or Form I and include a statement concerning this issue in the QA review.

X. COMPOUND QUANTITATION AND REPORTED QUANTITATION LIMITS

A. Review Items

QC summary forms, Case Narrative, integration reports, and chromatograms

B. Objective

The objective is to ensure that reported quantitative results and reported QLs are accurate.

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C. Criteria

1. Compound quantitation, as well as the adjustment of the QLs, must be calculated according to the correct equation specified in SW-846.

2. The compound quantitation must be based on the average CF from the initial calibration if the RSD is ≤20% or if the RSD is >20%, the initial calibration curve must be used for sample quantitation.

3. If Method 5030 is used, the sample must be analyzed with a heated purge.

D. Evaluation

1. Verify that the reported QLs are less than or equal to the QAPP-specified QLs. If sample dilution is necessary due to elevated target compound concentrations, or if interference related to the sample matrix is observed, the QLs reported by the laboratory may exceed required limits.

2. If Method 5030 was used, verify that the sample was analyzed with a heated purge.

3. For all samples, raw data should be examined to verify the correct calculation of all sample results reported by the laboratory. Integration reports and chromatograms should be compared to the reported positive sample results.

4. Verify that the correct CFs are used for quantitation. Verify that the same CFs are used consistently throughout, in both the calibration and the quantitation processes.

5. Verify that the QLs have been adjusted to reflect all sample dilutions that are not accounted for by the method.

E. Action

If QLs reported by the laboratory exceed the QAPP-specified QLs and no sample dilutions were necessary or matrix related interferences observed, professional judgment should be used to assess the validity of the elevated sample results. The problem should be noted as a comment in the QA review.
If the samples were not analyzed in the same manner as the calibration standards (i.e., the calibration was performed with a heated purge and the sample was not

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heated), the positive results should be considered estimated and flagged "J" and the "not-detected" results should be flagged "UJ".

If any discrepancies are found, the laboratory may be contacted by the designated representative to obtain additional information that could resolve any differences. If a discrepancy remains unsolved, the reviewer must use professional judgment to decide which value is the best value. Under these circumstances, the data reviewer may determine if qualification of data is warranted.

XI. FIELD DUPLICATES

A. Review Items

Analytical results forms, chromatograms, and integration reports

B. Objective

Field duplicates may be taken and analyzed as an indication of overall precision. These analyses measure both field and laboratory precision; therefore, the results may have more variability than laboratory duplicates, which measure only laboratory performance and matrix homogeneity. It is also expected that solid duplicate results will have a greater variability than the water matrices due to difficulties associated with collecting identical field samples.

C. Criteria

There are no specific review criteria for field duplicate analyses comparability. Refer to the site QAPP for project-specific requirements for sampling frequency and RPD.

D. Evaluation

Samples which are field duplicates should be identified in the QA review. The reviewer should compare the results reported for each sample and duplicate and calculate the RPD.

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E. Action

Positive results for a target compound should be flagged "J" in the sample and its duplicate if the following criteria are not met:

1. A control limit of ± 20% (± 40% for solids) for the RPD shall be used if both sample values are greater than 5× the QL.

2. A control limit of ± the QL (± 2× the QL for solids) for the difference between the duplicate results shall be used for sample values less than 5× the QL. If one of the results was a "not-detected" result, one half of the QL will be used as the sample value for the comparison between the results.

XII. SYSTEM PERFORMANCE

A. Review Items

QC summary forms and raw data.

B. Objective

During the period following instrument performance QC checks (e.g., blanks and calibrations), changes may occur in the analytical system that degrade the quality of the data. While this degradation would not be directly shown by QC checks until the next required series of analytical QC analyses, a thorough review of the ongoing data acquisition can yield indicators of instrument performance.

C. Criteria

There are no specific criteria for system performance. Professional judgment should be applied to assess the system performance.

D. Evaluation

1. Abrupt, discrete shifts in the chromatogram baseline may indicate a change in the instrument's sensitivity or the baseline setting. A baseline "shift" could indicate a decrease in sensitivity in the instrument or an increase in the instrument zero, possibly causing target compounds, at or near the detection limit, to miss detection. A baseline "rise" could indicate

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problems such as a change in the instrument zero, a leak, or degradation of the column.

2. Poor chromatographic performance affects both qualitative and quantitative results. Indications of substandard performance include:

   a. High background levels or shifts in absolute RTs for calibration standards.

   b. Excessive baseline rise.

   c. Extraneous peaks.

   d. Loss of resolution.

   e. Peak tailing or peak splitting that may result in inaccurate quantitation.

Error Action

Professional judgment must be used to qualify the data if it is determined that system performance has degraded during sample analyses.

XIII. OVERALL ASSESSMENT OF DATA

A. Review Items

Entire data package, data review results, QAPP, and Sampling and Analysis Plan

B. Objective

The overall assessment of a data package is a brief narrative in which the data reviewer expresses concerns and comments on the quality and, if possible, the usability of the data.

C. Criteria

Assess the overall quality of the data
Review all available materials to assess the overall quality of the data, keeping in mind the additive nature of analytical problems.

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D. Evaluation

1. Evaluate any technical problems which have not been previously addressed.

2. If appropriate information is available, the reviewer may assess the usability of the data to assist the client in avoiding inappropriate use of the data. Review all available information, including the QAPP, Sampling and Analysis Plan, and communications with the client that concerns the intended use and desired quality of these data.

E. Action

1. Use professional judgment to determine if there is any need to qualify data which were not qualified based on the QC previously discussed.

2. Prepare a fully-documented quality assurance review which provides the client with an indication of the analytical limitations of the data. If sufficient information on the intended use and required quality of the data are available, the reviewer should include an assessment of the usability of the data within the given context.

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XIV. AUTHORITY

This data validation SOP for the analysis for non-halogenated VOCs has been prepared by Environmental Standards, Inc. This SOP represents internal control copy _____ issued to _____ and is not to be photocopied or used by any other entity except Environmental Standards, Inc. without expressed written permission.

SOP approved by:

_____ Date: _____
Rock J. Vitale, CPC
Technical Director of Chemistry/Principal

Control Copy No.: _____

Received by: _____

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STANDARD OPERATING PROCEDURES FOR DATA VALIDATION OF POLYCHLORINATED DIBENZO-P-DIOXIN AND POLYCHLORINATED DIBENZOFURAN RESULTS GENERATED BY SW-846 METHOD 8280*

I. METHOD SUMMARY

Method 8280 provides matrix-specific extraction, analyte-specific cleanup, and high-resolution capillary gas chromatography/low-resolution mass spectrometry techniques for the analysis of polychlorinated dibenzo-*p*-dioxin (PCDDs) and polychlorinated dibenzofurans (PCDFs). This method is appropriate for chemical wastes, fuel oils, sludges, fly ash, soil, and water. Sample contamination can be attributed to the reagents, solvents, glassware, and other sample processing hardware used during the collection and analysis of the samples. Interfering compounds may be co-extracted from the sample, such as PCBs and other polychlorinated diphenyl ethers.

SW-846 methods allow for a considerable amount of laboratory interpretation in regard to the analytical requirements and data interpretation. Therefore, separate laboratories may perform the same method and utilize different acceptance criteria and different result interpretations. In addition, a project-specific QAPP might include requirements which differ from those presented in the SOP. Consequently, some of the sections in the SOP might not be applicable to all situations.

II. TECHNICAL HOLDING TIMES

A. Review Items

Analytical result pages, Chain-of-Custody records, raw data, and Case Narrative

B. Objective

The objective is to ascertain the validity of results based on the holding time of the sample from the time of collection to the time of analysis.

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* See Section XV for Authority and Application of this SOP.

C. Criteria

1. The extractions of aqueous samples are required to be performed within 30 days of the date of sample collection.

2. The extractions of solid samples are required to be performed within 30 days of the date of sample collection.

3. The analyses of sample extracts are required to be performed within 45 days of the date of sample collection.

4. The laboratory should record any observations concerning the samples upon receipt at the laboratory (i.e., sample containers cracked, etc.) on the Chain-of-Custody records.

5. The laboratory should record the temperature of the sample coolers (based upon the temperature of the temperature bottle) upon receipt at the laboratory on the Chain-of-Custody records or in a separate logbook. The temperature of the sample coolers are required to be maintained at 4±2°C. However, the data reviewer will not consider temperature issues to be a direct impact on the usability of PCDD/PCDF data.

D. Evaluation

Technical holding times are established by comparing the sampling dates on the Chain-of-Custody records with the dates of extraction and analysis on the sample analysis summary and raw data. Examine the sample records to determine if samples were properly preserved (cooled [4±2°C]).

E. Actions

1. If any criterion is exceeded, sample results will be qualified "R" or "UR" = unusable, "J" = estimated, "UJ" = quantitation limit [QL] is biased, "A" = professional judgment as defined in [2]) by the data reviewer according to the following table:

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Qualification Due to Exceeded Holding Times			
Holding Time for:	Days Beyond Collection/ Extraction Date	Positive Result(s)	"Not-Detected" Result(s)
Aqueous Sample Extraction	31-60 days > 60 days	"A" "J"	"UJ" "UR"
Solid Sample Extraction	31-60 days > 60 days	"A" "J"	"UJ" "UR"
Extract Injection	46-90 days > 90 days	"J" "A"	"UJ" "UR"

2. If the extraction holding time criterion is exceeded by 31 to 60 days beyond the date of collection, a comment will be written in the quality assurance report (QAR) by the data reviewer addressing the fact that extracting the sample beyond the holding time may lead to a loss of analyte; however, in the opinion of the data reviewer, data should not be impacted due to the extreme stability of the PCDD/PCDF compounds.

3. If observations such as cracked containers were noted on the Chain-of-Custody Records, a comment will be written in the QAR by the data reviewer addressing the fact that these issue(s) may lead to a loss of analyte. Professional judgment will be used to determine if the severity of the problem warrants qualification.

4. If the temperature of the temperature bottle (or an IR gun temperature measurement of a sample bottle) upon receipt at the laboratory was greater than 6°C, a comment will be written in the QAR by the data reviewer addressing the fact that elevated temperatures may lead to a loss of analyte; however, in the opinion of the data reviewer, data should not be impacted due to the stability and chemical properties (i.e., vapor pressure, boiling point, etc.) of the PCDD/PCDF compounds.

5. If the laboratory recorded the air temperature of the cooler rather than a sample bottle temperature, note in the quality assurance review that this method of determining cooler temperature may not be indicative of sample temperature.

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III. WINDOW DEFINING MIXTURE (DB5 COLUMN)

A. Review Items

Calibration summary forms, integration reports, and chromatograms

B. Objective

Compliance requirements for instrument separation are established to ensure that the instrument is capable of producing acceptable qualitative and quantitative data for the PCDDs and PCDFs.

C. Criteria

1. The laboratory is required to analyze the Window Defining Mixture containing the first and last eluting isomers in each congener class of dioxin and furan compounds and the compounds 2,3,7,8-TCDD and 1,2,3,4-TCDD at a frequency of once prior to the initial calibration, once per day (12 hr.), prior to the continuing calibration, once when adjustments or instrument maintenance activities that may affect retention times are performed, or whenever a significant change in retention time (±10 sec.) of the target analytes has been observed. The retention times of the first and last eluting isomers are used to establish the retention time windows for each congener class of dioxin and furan compounds. The percent valley between the compounds 2,3,7,8-TCDD and 1,2,3,4-TCDD is required not to exceed 25%, where:

$$\text{Percent Valley} = (x/y)\ (100\%)$$

x = the height of the valley (from baseline to valley)
y = the peak height of 2,3,7,8-TCDD

2. The retention times of all compounds in the continuing calibration standards are required to be within the retention time windows established prior to the continuing calibration at the beginning of the day. See Section VI of this SOP for frequency and additional requirements for continuing calibration standards.

3. At a minimum, the Window Defining Mixture must contain 2,3,7,8-TCDD and 1,2,3,4-TCDD, and the following (first eluting; last eluting) isomers:

TCDD	1,3,6,8; 1,2,8,9;
PeCDD	1,2,4,7,9; 1,2,3,8,9;
HxCDD	1,2,4,6,7,9; 1,2,3,4,6,7;
HpCDD	1,2,3,4,6,7,9; 1,2,3,4,6,7,8;
TCDF	1,3,6,8; 1,2,8,9;
PeCDF	1,3,4,6,8; [illegible]
HxCDF	1,2,3,4,6,8; 1,2,3,4,8,9; and
HpCDF	1,2,3,4,6,7,8; 1,2,3,4,7,8,9.

Note: The 1,2,3,4,7,8-HxCDD and 1,2,3,6,7,8-HxCDD isomers may also be present in the Window Defining Mixture.

D. Evaluation

1. Verify that a Window Defining Mix was analyzed on all of the instruments used for analysis.

2. Verify that the percent valley between 2,3,7,8-TCDD and 1,2,3,4-TCDD was calculated correctly.

3. Verify that the retention times are within the retention time windows established by the continuing calibration standard.

4. Verify that the Window Defining Mix contains the appropriate congeners.

E. Action

1. If the Window Defining Mixture was not analyzed at the required frequency, professional judgment will be used by the data reviewer to determine the affect on the data quality.

2. If the percent valley between the compounds 2,3,7,8-TCDD and 1,2,3,4-TCDD is greater than 25%, positive results for the 2,3,7,8-TCDD isomer may be affected and should be flagged as estimated ("J") by the data reviewer. One of the following two options will be followed:

   a. If the 2,3,7,8-TCDD concentration was reported from the analysis with resolution problems, the result will be flagged as estimated ("J") by the data reviewer.

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b. If the 2,3,7,8-TCDD concentration was not reported from the analysis with resolution problems, but was reported from a confirmation analysis on the SP2331 column with acceptable resolution, no further action or qualification will be necessary.

3. If the retention time of any compound in the Window Defining Mixture is outside the corresponding retention time window established at the beginning of the day by more than ±10 seconds, the sample data since the last compliant Window Defining Mixture and associated with the noncompliant Window Defining Mixture, will be evaluated by the data reviewer as follows:

a. If there are no reported positive results associated with the noncompliant or the last compliant Window Defining Mixtures, some peaks which meet all other identification criteria except the retention time window criterion are potentially affected. If there are no other peaks, no further action or qualification will be necessary.

b. If there are reported positive results and no tentative positives (peaks as described above), no further action or qualification will be necessary.

c. If there are potential positives (peaks as described above) for either a or b, these peaks will be evaluated by data reviewer to determine if the peaks are within an adjusted retention time window. If any peak meets all of identification criteria and is within the adjusted retention time window, the resulting concentration may be reported (at the discretion of the data reviewer) as a positive result and flagged "N". The "N" signifies that the compound has been identified with presumptive evidence.

IV. COLUMN PERFORMANCE SOLUTION MIXTURE (SP2331 COLUMN)

A. Review Items

Calibration summary forms, integration reports, and chromatograms

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B. Objective

Compliance requirements for satisfactory instrument separation are established to ensure that the instrument is capable of producing acceptable qualitative and quantitative data for the PCDDs and PCDFs.

C. Criteria

1. The laboratory was required to analyze the Column Performance Solution Mixture (CPSM) containing the TCDD isomers that elute most closely with the 2,3,7,8-TCDD isomer (1,2,3,8-TCDD and 1,2,3,7/1,2,3,8-TCDD pair) at a frequency of once prior to the analysis of initial and continuing calibration standards. The percent valley between unlabelled 2,3,7,8-TCDD and all other unlabelled TCDD isomers is required not to exceed 25%, where:

   Percent Valley = (x/y) (100%)

   x = the height of the valley (from baseline to valley)
   y = the peak height of 2,3,7,8-TCDD

2. The CPSM must contain the following TCDD isomers:

   1,4,7,8-TCDD
   2,3,7,8-TCDD
   1,2,3,7/1,2,3,8-TCDD
   1,2,3,4-TCDD
   1,2,3,6,4-TCDD
   ^{13}C-2,3,7,8-TCDD

D. Evaluation

1. Verify that a CPSM was analyzed on all of the instruments used for analysis.

2. Verify that the percent valley between 2,3,7,8-TCDD and all other unlabelled TCDDs were calculated correctly.

3. Verify that the retention times were within the retention time windows established by the continuing calibration standard.

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4. Verify that the CPSM contains the appropriate congeners.

E. Action

1. If the CPSM was not analyzed at the required frequency, or did not contain the appropriate TCDD congeners, professional judgment will be used by the data reviewer to determine the effect on the data quality.

2. If the percent valley between the unlabelled 2,3,7,8-TCDD and all other unlabelled TCDD isomers is greater than 25%, positive results for the 2,3,7,8-TCDD isomer will be rejected and will be flagged as estimated ("J") by the data reviewer.

3. If the TCDD congeners did not elute within the specified retention time windows, professional judgment will be used to determine the effect on data quality.

V. INITIAL CALIBRATION

A. Review Items

Calibration summary forms, integration reports, and chromatograms

B. Objective

Compliance requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable qualitative and quantitative data for PCDFs and PCDDs.

C. Criteria

1. For all toxic dioxin and furan isomers (i.e., those isomers which have chlorine atoms at the 2, 3, 7, and 8 positions on the aromatic rings), internal standards, and the recovery standard, a five-point calibration was required at the beginning of the analytical sequence. The standard concentrations were required to be those specified in the analytical method.

2. The percent relative standard deviation (%RSD) of response factors (calculated using peak area) from the five-point initial calibration was required to be less than or equal to 15%.

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3. The relative ion abundance ratios for the quantitation and the secondary ions of the target analytes, internal standards, and recovery standard are required to be within the acceptable ranges specified below:

Relative Ion Abundance Criteria PCDDs and PCDFs

PCDDs	Selected ions (m/z)	Relative intensity
Tetra	320/322	0.65-0.89
Penta	356/358	1.24-1.86
Hexa	390/392	1.05-1.43
Hepta	424/426	0.88-1.20
Octa	458/460	0.76-1.02

PCDFs	Selected ions (m/z)	Relative intensity
Tetra	304/306	0.65-0.89
Penta	340/342	1.24-1.86
Hexa	374/376	1.05-1.43
Hepta	408/410	0.88-1.20
Octa	442/444	0.76-1.02

4. The retention times of all target analytes, internal standards, and recovery standards are required to be within the appropriate retention time windows established with the Window Defining Mixture analysis.

5. The three monitored ions for each native isomer are required to be present and maximize simultaneously within three seconds of the corresponding ^{13}C-labeled compound.

6. The signal to noise ratio (S/N) for the unlabelled PCDD/PCDF ions is required to be greater than 2.5.

7. The signal to noise ratio (S/N) for the internal standard and recovery standard ions as required to be greater than 10.

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8. The signal to noise ratio (S/N) for the m/z 320 ion of 2,3,7,8-TCDD in the mid-level initial calibration standard is required to be greater than 50 to 1.

D. Evaluation

1. Verify that the concentrations of the standards that were used for the initial calibration were based on the QAPP.

2. Verify that the correct initial calibration was used for all samples.

3. Verify that the sample results were calculated correctly. Specifically, if the RSD is ≤15%, the average response factor (RRF) from the initial calibration should be used. If the RSD >15%, corrective action must be taken and the instrument must be recalibrated.

4. Evaluate the initial calibration RRFs for all target compounds.

   a. Check and recalculate the RRFs and average RRF for at least three target compounds; verify that the recalculated value(s) agrees with the laboratory-reported value(s). If errors are detected in the calibrations, perform a more comprehensive recalculation.

   b. Verify that the relative ion abundance ratios for the quantitation and the secondary ions of the target analytes, internal standards, and recovery standards are within the limits specified in Section V.C.3 above.

5. Evaluate the RSD for all target compounds.

   a. Check and recalculate the RSD for one or more target compound(s); verify that the recalculated value(s) agrees with the laboratory-reported value(s). If errors are detected in the calculations, perform a more comprehensive recalculation.

   b. Verify that all target compounds have a RSD less than or equal to 15%.

6. Verify that the retention times of several target analytes, internal standards, and recovery standard peaks were within the appropriate retention time windows.

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7. Verify that the monitored ions for each native isomer are present and maximize within three seconds of the corresponding ^{13}C-labeled compound.

8. Verify that all of the signal to noise ratios are greater than the minimum ratios of 2.5:1 for unlabeled PCDD/PCDF ions, 10:1 for the internal standards and recovery standard ions, and 50:1 for the m/z 320 ion of 2,3,7,8-TCDD in the mid-standard.

E. Action

1. If the %RSD of the response factors (calculated using peak area) from the five-point initial calibration was greater than 15%, data will be qualified by the data reviewer as follows:

   a. Associated positive results will be flagged as estimated ("J").

   b. Associated "not-detected" results (calculated detection limits) will be qualified as biased ("UB") for 50% ≤ %RSD ≤ 90% and unusable ("UR") for %RSD > 90%.

2. If the relative ion abundance ratio for the quantitation and the secondary ions of the target analytes, internal standards, and/or recovery standard was not within the acceptable ranges listed above, the affected analyte data will be flagged as unusable ("R" or "UR") by the data reviewer.

3. If the retention time of any target analyte, internal standard, and/or recovery standard was not within the appropriate retention time windows (±10 sec.) established with the Window Defining Mixture analysis, the affected analyte data will be flagged as unusable ("R" or "UR") by the data reviewer.

4. If the three monitored ions for a native isomer were not present and/or did not maximize simultaneously within three seconds of the corresponding ^{13}C-labeled compound, the data reviewer will take action as follows:

   a. If the result in question had been reported as a positive result, the data reviewer will change the reported positive result to a "not-detected" result. The reported concentration is reported as the detection limit. This action will be summarized in a comment in the QAR.

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b. If the result in question had been reported as a maximum possible concentration (MPC) result, the data reviewer will change the reported MPC result to a "not detected" result. The reported MPC concentration is reported as the detection limit. This action will be summarized in a comment in the QAR.

5. If the signal to noise ratio (S/N) for any unlabelled PCDD/PCDF ion is less than 2.5, the detection limits for these unlabelled PCDDs/PCDFs are flagged as biased ("UJ") by the data reviewer.

6 If the signal to noise ratio (S/N) for any internal standard and/or recovery standard ion is less than 10, the detection limits for the associated PCDDs/PCDFs are flagged as biased ("UJ") by the data reviewer.

7. If the signal to noise ratio (S/N) for the m/z 320 ion of 2,3,7,8-TCDD in the mid-initial calibration standard is less than 50, the detection limits for 2,3,7,8-TCDD are flagged as biased ("UJ") by the data reviewer.

VI. CONTINUING CALIBRATIONS

A. Review Items

Calibration summary forms, integration reports, and chromatograms

B. Objective

Continuing calibrations are performed to verify that the initial calibration curve is still valid for the quantitation of results with respect to sensitivity and accuracy on a day-to-day basis.

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C. Criteria

1. Within 12 hours prior to the analysis of samples and following the WDM analysis, a mid-level continuing calibration standard containing all toxic dioxin and furan isomers (i.e., those isomers which have chlorine atoms at the 2, 3, 7, and 8 positions on the aromatic rings), all internal standards, and the recovery standard are required to be analyzed.

2. The absolute value of the percent differences (|%D|) between the measured RRFs and the average RRF calculated from the initial calibration are required to be less than or equal to 30%.

3. The relative ion abundance ratios for the quantitation and the secondary ions of the target analytes, internal standards, and recovery standard are required to be within the acceptable ranges specified below:

Relative Ion Abundance Criteria PCDDs and PCDFs

PCDDs	Selected ions (m/z)	Relative intensity
Tetra	320/322	0.65-0.89
Penta	356/358	1.24-1.86
Hexa	390/392	1.05-1.43
Hepta	424/426	0.88-1.20
Octa	458/460	0.76-1.02

PCDFs	Selected ions (m/z)	Relative intensity
Tetra	304/306	0.65-0.89
Penta	340/342	1.24-1.86
Hexa	374/376	1.05-1.43
Hepta	408/410	0.88-1.20
Octa	442/444	0.76-1.02

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4. The retention times of all target analytes, internal standards, and recovery standard are required to be within the appropriate retention time windows established with the Window Defining Mixture analysis.

5. The three monitored ions for each native isomer are required to be present and maximize simultaneously within three seconds of the corresponding ^{13}C-labeled compound.

6. The signal to noise ratio (S/N) for the unlabelled PCDD/PCDF ions is required to be greater than 2.5.

7. The signal to noise ratio (S/N) for the internal standard and recovery standard ions is required to be greater than 10.

8. The signal to noise ratio (S/N) for the m/z 320 ion of 2,3,7,8-TCDD in the low initial calibration standard is required to be greater than 50.

D. Evaluation

1. Verify that the continuing calibration was run at the required frequency and that the continuing calibration was compared to the correct initial calibration.

2. Evaluate the continuing calibration recovery for all target compounds:

   a. Quantitatively verify that the recovery was calculated properly; verify that the recalculated value(s) agrees with the laboratory-reported value(s). If errors are detected in the calculation of the results, perform a more comprehensive recalculation.

   Verify that the relative ion abundance ratios for the quantitation and the secondary ions of the target analytes, internal standards, and recovery standard were calculated properly; verify that the recalculated value(s) agrees with the laboratory-reported value(s). If errors are detected in the calculation of the results, perform a more comprehensive recalculation.

3. Evaluate the percent recovery between the expected result and the observed result for all compounds.

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a. Check and recalculate the percent recovery for at least three target compounds; verify that the recalculated value(s) agrees with the laboratory-reported value(s). If errors are detected in the calculation of the recovery, perform a more comprehensive recalculation.

b. Verify that the percent recovery is within the acceptance limits for all target compounds.

4. Verify that the retention time of the target analytes, internal standards, and recovery standard are within retention time windows.

5. Verify that the three monitored ions for each isomer maximize within three seconds of the corresponding ^{13}C-labeled compound.

6. Verify that all of the signal-to-noise ratios are greater than the minimum ratios of 2.5:1 for unlabelled PCDD/PCDF ions, 10:1 for the internal standards and recovery standard ions, and 50:1 for the m/z 320 ion of 2,3,7,8-TCDD in the mid-level standard.

E. Action

1. For the dioxin and furan target analytes, if a continuing calibration standard was not performed within 12 hours prior to a sample analysis, all affected data is flagged as unusable ("R" or "UR") by the data reviewer.

2. If the absolute value of the %D (|%D|) of any of the RRFs (calculated using peak area) calculated for the continuing calibration as compared to the average RRFs calculated from the five-point initial calibration was greater than 30%, data will be qualified by the data reviewer as follows:

a. Associated positive results will be flagged as estimated ("J").

b. Associated "not-detected" results (calculated detection limits) will be qualified as biased ("UJ") for 30% ≤ |%D| ≤ 90%, and unusable ("UR") for |%D| > 90%.

3. If the relative ion abundance ratio for the quantitation and the secondary ions of the target analytes, internal standards, and/or recovery standard was not within the acceptable ranges listed above, the affected analyte data will be flagged as unusable ("R" or "UR") by the data reviewer.

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4. If the retention time of any target analyte, internal standard, and/or recovery standard was not within the appropriate retention time windows (±10 sec.) established with the Window Defining Mixture analysis, the affected analyte data will be flagged as unusable ("R" or "UR") by the data reviewer.

5. If the three monitored ions for a native isomer were not present and/or did not maximize simultaneously within three seconds of the corresponding ^{13}C-labeled compounds, the data reviewer will take actions as follows:

   a. If the result in question was reported as a positive result, the data reviewer will change the reported positive result to a "not-detected" result. The reported concentration is reported as the detection limit. This action will be summarized in a comment in the QAR.

   b. If the result in question was reported as a maximum possible concentration (MPC) result, the data reviewer will change the reported MPC result to a "not-detected" result. The reported MPC concentration is reported as the detection limit. This action will be summarized in a comment in the QAR.

6. If the signal to noise ratio (S/N) for any unlabelled PCDD/PCDF ion is not greater than 2.5, the detection limits for these unlabelled PCDDs/PCDFs are flagged as biased ("UJ") by the data reviewer.

7. If the signal to noise ratio (S/N) for any internal standard and/or recovery standard ion is not greater than 10, the detection limits for the associated PCDDs/PCDFs are flagged as biased ("UJ") by the data reviewer.

8. If the signal to noise ratio (S/N) for the m/z 320 ion of 2,3,7,8-TCDD in the calibration standard is not greater than 50, the affected positive results will be flagged as estimated ("J") and the detection limits for 2,3,7,8-TCDD are flagged as biased ("UJ") by the data reviewer.

VII. BLANKS

A. Review Items

QC summary forms, chromatograms, and integration reports

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B. Objective

The assessment of blank analysis results determines the existence and magnitude of contamination problems. The criteria for the evaluation of blanks apply to any type of blank associated with the samples. If problems with any blank exist, all associated data must be carefully evaluated to determine whether or not there is an inherent variability in the data or if the problem is an isolated occurrence not affecting the other data.

C. Criteria

1. The preparation and analysis of a method blank is required for every 20 samples of a similar matrix and/or every time samples are extracted, whichever is more frequent.

2. The collection of field blanks may be required for most sampling events. The applicable work plan or sampling plan will be consulted for the required collection frequency and applicability.

3. In order to rule out any possible impact on data usability, positive results for the target compounds should not be observed for any blank.

D. Evaluation

1. Review the results of all associated blanks on the forms and raw data (chromatograms and integration reports) to evaluate the presence of target compounds in the blanks.

2. Verify that a method blank analysis has been reported for each day, each extraction batch, and on each instrument used to analyze samples.

E. Action

1. If the appropriate blanks were not analyzed with the frequency described above (Section VII.C.1 and 2), professional judgment will be used by the data reviewer to determine if qualification of the associated data is necessary.

2. If a PCDD/PCDF isomer is detected in a sample analysis and is also detected in the analysis of any associated blank (see [3], below, for what blanks are associated with the samples), the positive results will be

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qualified according to the 5-times rule (10-times for OCDD) by the data reviewer as shown in the following table:

Qualification by the 5-times (10-times for OCDD) Rule* for Blank Contamination	
If:	Then:
DL < Sample Concentration < 5× (10× for OCDD) Blank Concentration	Flag Sample Result with a 'U'
Sample Concentration > DL and > 5× (10× for OCDD) Blank Concentration	No Qualification of Data is Needed

Note: It should be noted that blanks may not involve the same weights, volumes, dilution factors, and/or dry-weight correction factors as the associated samples. These factors must be taken into consideration when applying the 5-times (or 10-times) criterion. This is generally best accomplished by directly comparing the concentrations at the instrument levels.

3. The results of all laboratory method blanks will be used by the data reviewer to flag all samples of a matrix similar to the method blank matrix in the Sample Delivery Group (SDG). The data reviewer will use the results of a field blank to flag all samples collected on the same day (unless only one was collected for a several day sampling event; field blank results would then be applied to all samples in the SDG).

4. If a PCDD/PCDF isomer is found in a blank but not in the sample, no action will be taken by the data reviewer. However, if a class of contaminants (e.g., TCDDs) was detected in field blanks but not in the samples, a comment addressing this issue will be written in the QAR by the data reviewer.

5. If it is determined that contamination has been introduced from a source other than the sample, qualification of data may be made by the data reviewer. Contamination introduced through dilution water is one example. Instances of this occurring can be identified when compounds have been detected in the diluted sample but not in the undiluted sample.

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6. Professional judgment by the data reviewer will be utilized when a peak observed in the blank chromatogram is within the retention time window of a target compound and is reported as a maximum possible concentration (MPC). Sample chromatograms will be examined closely in comparing such peaks. If similar peaks are observed in the blank and associated samples within the retention time window of target compounds, it will be noted that certain positive results should be used with caution. In addition, when warranted as determined by professional judgment, such positive results may be qualified as "not detected" ("U").

VIII. INTERNAL STANDARDS

A. Review Items

QC summary forms, integration reports, and chromatograms

B. Objective

Laboratory performance (accuracy) in individual samples and blanks is established by means of spiking activities. All samples and blanks are spiked with the internal standard compounds prior to sample extraction. Recovery standards are spiked into sample extracts just prior to analysis.

C. Criteria

1. All standards, blanks, field samples, and quality control samples are required to be spiked with a mixture of ^{13}C-labeled compounds including ^{13}C-2,3,7,8-TCDF, ^{13}C-2,3,7,8-TCDD, ^{13}C-1,2,3,7,8-PeCDD, [illegible] ^{13}C-1,2,3,6,7,8-HxCDD, ^{13}C-1,2,3,4,6,7,8-HpCDD, and ^{13}C-OCDD. Percent recoveries (%Rs) for these compounds are required to be calculated and must be greater than 40%, or the signal to noise ratio must be greater than 10.

2. The relative ion abundance ratios for the quantitation and the secondary ions of the internal standards and recovery standard were required to be within the acceptable ranges specified below:

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Relative Ion Abundance Criteria PCDDs and PCDFs

PCDDs	Selected ions (m/z)	Relative intensity
Tetra	320/322	0.65-0.89
Penta	356/358	1.24-1.86
Hexa	390/392	1.05-1.43
Hepta	424/426	0.88-1.20
Octa	458/460	0.76-1.02

PCDFs	Selected ions (m/z)	Relative intensity
Tetra	304/306	0.65-0.89
Penta	340/342	1.24-1.86
Hexa	374/376	1.05-1.43
Hepta	408/410	0.88-1.20
Octa	442/444	0.76-1.02

3. The retention times of all of the internal standards and the recovery standard are required to be within the appropriate retention time windows established with the Window Defining Mixture analysis.

D. Evaluation

1. Verify that internal standard compounds were added to all samples and blanks.

2. Verify that the laboratory calculated the relative ion abundance ratios, percent recoveries, and signal to noise ratio values correctly.

3. If any internal standard compound is outside the acceptance criteria (laboratory-specified), there should be a reanalysis to confirm that the noncompliance is due to sample matrix effects rather than laboratory deficiencies.

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4. Verify that the retention times of the internal standards and recovery standard are within the appropriate retention time windows as established by the WDM analysis.

E. Action

1. If the percent recovery (%R) for any internal standard is less than 40% and the signal to noise ratio is greater than or equal to 10, no further action or qualification is necessary.

2. If the percent recovery (%R) for any internal standard is less than 40% and the signal to noise ratio is less than 10, the results for compounds quantitated with that internal standard will be qualified by the data reviewer as follows:

   a. Positive results for the affected analytes will be flagged as estimated ("J").

   b. The detection limits for the affected analytes will be flagged as biased ("UJ").

3. If the relative ion abundance ratio for the quantitation and the secondary ions of any of the internal standards or the recovery standard was not within the acceptable ranges specified above (Section VIII.C.2), professional judgment will be used by the data reviewer to determine if qualification of the associated data is necessary.

4. If the retention times of any of the internal standards or the recovery standard varied by more than 10 seconds or were not within the acceptable retention time windows established with the Window Defining Mixture analysis, professional judgment will be used by the data reviewer to determine if qualification of the associated data is necessary.

IX. MATRIX SPIKES/MATRIX SPIKE DUPLICATES/BLANK SPIKES (OR LABORATORY CONTROL SAMPLES)

A. Review Items

QC summary forms, chromatograms, and integration reports

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B. Objective

Data for matrix spikes (MSs)/matrix spike duplicates (MSDs) are generated to determine long-term accuracy and precision of the analytical method on various matrices and to demonstrate acceptable compound recovery by the laboratory at the time of sample analysis. These data alone are not used to evaluate the accuracy of other samples. The data for blank spikes (BSs) or Laboratory Control Samples (LCSs) are generated to determine analytical accuracy. The results of blank spikes are used to assess the accuracy of the entire sample batch.

C. Criteria

1. The preparation of a matrix spike (MS) and a matrix spike duplicate (MSD) of a project sample is required for every 20 samples of a similar matrix. All toxic isomers of dioxin and furan (i.e., those isomers which have chlorine atoms at the 2, 3, 7, and 8 positions on the aromatic rings) are required to be in each spike.

2. The MS/MSD results are required to be quantitated in the same manner as the samples. All MS/MSD spike compound percent recoveries (see note below) should be within the data usability limits of 50-150% recovery for data not to be potentially impacted. The relative percent differences (RPDs) between the results for each compound in the MS and MSD should be less than or equal to 50% for the data not to be potentially impacted.

3. The preparation of a laboratory control sample (LCS) is required for every 20 samples of a similar matrix and/or every time samples are extracted, whichever is more frequent.

4. The LCS results are required to be quantitated in the same manner as samples. If the LCS did not meet the recovery criteria, all associated samples are required to be reextracted and reanalyzed. However, all LCS spike compound recoveries should be within the data usability limits of 50-150% for the data not to be potentially impacted.

5. The spike compounds are required to satisfy all of the identification criteria that are applied to sample and blank results.

Note: Since the quantity of spiked compound recovered is corrected for the recovery of the associated internal standard, the correct term is

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"percent accuracy." However, to remain consistent with the laboratory's nomenclature, the term "percent recovery" will be used.

D. Evaluation

1. Verify that an MS/MSD and BS (or LCS) were analyzed at the required frequency.

2. Inspect results for the MS/MSD/BS (or LCS) recoveries and MS/MSD RPDs on the QC summary forms and verify that the results for the recoveries are within the specified limits.

3. Verify transcriptions from raw data and verify calculations.

4. Compare RPD results of nonspiked compounds between the unspiked result and the MS/MSD results.

5. Verify that the MS/MSD results meet the identification criteria (Section X) and quantitation criteria (Section XI).

E. Action

1. If the recovery for any compound did not meet the limits of 50-150% in the MS and/or MSD analyses, the result for that compound in the **unspiked sample only** will be qualified by the data reviewer according to the following table.

Qualification Due to Poor MS/MSD Recoveries			
If Percent Recovery (%R):	and Signal to Noise (S/N) Ratio:	Flag Positive Result:	Flag "Not-Detected" Result:
%R < 10%	≥ 10	"J"	"UJ"
%R < 10%	< 10	"J"	"UR"
10% ≤ %R < 50%	≥ 10	"J"	No Qualification
10% ≤ %R < 50%	< 10	"J"	"UJ"
%R > 150%	≥ 10	"J"	No Qualification
%R > 150%	< 10	"J"	"UJ"

2. If the RPD between the results for any compound in the matrix spike and matrix spike duplicate exceeded 50%, positive results for that compound in

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the unspiked sample only will be qualified as estimated ("J") by the data reviewer.

3. If the recovery for any compound does not meet the limits of 50-150% in the LCS analysis, the results for that compound in **all associated samples** will be qualified by the data reviewer according to the following table:

Qualification Due to Poor LCS Recoveries			
If Percent Recovery (%R):	And Signal to Noise (S/N) Ratio:	Flag Positive Results:	Flag "Not Detected" Results:
%R < 10%	≥ 10	"J"	"UJ"
%R < 10%	< 10	"J"	"UR"
10% ≤ %R < 50%	≥ 10	"J"	No Qualification
10% ≤ %R < 50%	< 10	"J"	"UJ"
%R > 150%	≥ 10	"J"	No Qualification
%R > 150%	< 10	"J"	"UJ"

4. If any of the spike compounds did not satisfy all of the identification criteria specified for samples and blanks, professional judgment will be used by the data reviewer to determine if qualification of the associated data is necessary.

X. COMPOUND IDENTIFICATION

A. Review Items

QC summary forms, Case Narrative, integration reports, and chromatograms

B. Objective

The objective is to ensure that reported results are qualitatively accurate.

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C. Criteria

1. A toxic dioxin or furan isomer (i.e., those isomers that have chlorine atoms at the 2, 3, 7, and 8 positions on the aromatic rings) is required to be considered identified if the following conditions are satisfied:

   a. All of the characteristic ions (i.e., quantitation ions and confirmation ions) listed in the method for each class of PCDD and PCDF must be present in the reconstructed ion chromatogram. It is required that the M-COCl ion be monitored. Detection limits are based on quantitation ions within the molecule's fragment cluster. For a positive identification, all ions must have a signal to noise (S/N) ratio of 2.5:1.

   b. The three monitored ions for each native isomer are required to be present and maximize simultaneously (within 2 scans or 2 seconds) with the corresponding ^{13}C-labeled compound.

   c. The relative ion abundance ratios for the quantitation and the secondary ions of the target analytes must be within the acceptable ranges specified below.

Relative Ion Abundance Criteria PCDDs and PCDFs

PCDDs	Selected ions (m/z)	Relative intensity
Tetra	320/322	0.65-0.89
Penta	356/358	1.24-1.86
Hexa	390/392	1.05-1.43
Hepta	424/426	0.88-1.20
Octa	458/460	0.76-1.02

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PCDFs	Selected ions (m/z)	Relative intensity
Tetra	304/306	0.65-0.89
Penta	340/342	1.24-1.86
Hexa	374/376	1.05-1.43
Hepta	408/410	0.88-1.20
Octa	442/444	0.76-1.02

d. The retention times of the three monitored ions must be within the appropriate retention time windows established with the Window Defining Mixture analysis.

2. If a GC peak with S/N greater than 2.5 is detected at the same retention time as a PCDF peak in the corresponding polychlorinated diphenylether (PCDPE) channel, the identification of the peak as a PCDF cannot be made. The laboratory is required to report the calculated concentration as a Maximum Possible Concentration (MPC), regardless of the ion abundance ratio, and to note the identification in the Case Narrative.

3. Confirmation on the SP2331 column may have been performed if any 2,3,7,8 isomers in the *tetra-* through *hexa-* chlorination were detected in the DB5 analysis of the sample.

D. Evaluation

1. Verify the presence, signal to noise ratio of all of the monitored ions, and the relative ion abundances.

2. Verify the absence of the PCDPE peak for the identification of PCDFs.

3. Verify that a confirmation analysis was performed on a SP2331 column for any identified 2,3,7,8 isomers in the *tetra-* through *hexa*-chlorinated cogneres.

E. Actions

1. If any of the identification criteria specified above were not met for a reported positive result, the data reviewer will take the following actions depending on which and how many criteria were not satisfied:

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a. If more than one criterion was not met for a reported positive result, the result will be changed to "not detected" and a detection limit will be determined by the data reviewer.

b. If only one criterion was not met for a reported result, professional judgment will be used by the data reviewer to determine if the result should be changed from a reported positive result to a "not-detected" result, or an MPC.

2. If a GC peak was present in the corresponding PCDPE channel at the same retention time as a reported PCDF result, the result will be flagged as unusable ("R" or "UR") by the data reviewer.

XI. COMPOUND QUANTITATION AND REPORTED QUANTITATION LIMITS

A. Review Items

QC summary forms, Case Narrative, integration reports, and chromatograms

B. Objective

The objective is to ensure that reported quantitative results and reported quantitation limits (QLs) are accurate.

C. Criteria

1. All quantitations must be based on the response factors determined from the continuing calibration performed within 12 hours prior to sample [illegible]

2. All quantitations must be based on the internal standards and quantitation ions specified in the analytical method.

3. All quantitations (positive results and calculated detection limits) must be based on the correct equation specified in the analytical method. Solid sample results must be reported on a dry-weight basis.

4. All quantitations for 2,3,7,8-isomers must be based on the results obtained from the confirmation analysis on the SP2331 column.

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5. All quantitations that are below the concentration of the low calibration standard are reported as estimates by the laboratory.

D. Evaluation

1. Verify that the reported QLs are less than or equal to the QAPP-specified QLs. If sample dilution is necessary due to elevated target compound concentrations, or if interference related to the sample matrix is observed, the QLs reported by the laboratory may exceed required limits.

2. Verify that the sample was analyzed within 12 hours of the continuing calibration standard analyses.

3. For all samples, raw data should be examined to verify the correct calculations of all sample results reported by the laboratory. Integration reports and chromatograms should be compared to the reported positive sample results.

4. Verify that the correct RRFs are used for quantitation. Verify that the same RRFs are used consistently throughout, in both the calibration and the quantitation processes.

5. Verify that the QLs have been adjusted to reflect all sample dilutions that are not accounted for by the method.

E. Action

1. If the reported results were not based on all of the above-listed items, the laboratory will be requested by the data reviewer to perform corrective action and resubmit the affected data. An exception may be made if the data reviewer can perform the corrective action in a timely manner.

2. All concentrations that are below the concentration of the low calibration standard will be reported as an estimate and will be flagged "J" by the data reviewer.

3. If a discrepancy remains unresolved, the data reviewer must exercise professional judgment to decide which value is the best value and if qualification of data is warranted. If the quantitation limits reported by the laboratory exceed project-quantitation limits (or regulatory limits), and no sample dilutions were necessary or matrix-related interference was not

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observed, professional judgment will be exercised to assess the validity of the elevated sample results. The problem should be noted in the QAR.

XII. FIELD DUPLICATES

A. Review Items

Analytical result forms, chromatograms, and integration reports

B. Objective

Field duplicates may be taken and analyzed as an indication of overall precision. These analyses measure both field and laboratory precision; therefore, the results may have more variability than laboratory duplicates, which measure only laboratory performance and matrix homogeneity. It is also expected that solid duplicate results will have a greater variability than the water matrices due to difficulties associated with collecting identical field samples.

C. Evaluation

1. The low-standard concentration expressed as a sample result (including sample volumes/weights, dilution, etc.) will be considered the PCDD/PCDF quantitation limit (QL) for field duplicate evaluation. The relative percent difference between the results in aqueous field duplicates should be less than or equal to 20% for results greater than 5× the QL. The difference between results in aqueous field duplicates should be less than the QL when at least one result is less than or equal to 5× the QL.

2. The low-standard concentration expressed as a sample result (including sample volumes/weights, dilution, etc.) will be considered the PCDD/PCDF quantitation limit (QL) for field duplicate evaluation. The relative percent difference between the results in soil field duplicates should be less than or equal to 40% for results greater than 5× the QL. The difference between results in soil field duplicates should be less than 2× the QL when at least one result is less than or equal to 5× the QL.

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D. Actions

If the results for any compounds do not meet the above criteria, the positive results for this compound in the field duplicate pair will be flagged "J" by the data reviewer.

XIII. SYSTEM PERFORMANCE

A. Review Items

QC summary forms and raw data

B. Objectives

During the period following instrument performance QC checks (e.g., blanks and calibrations), changes may occur in the analytical system that degrade the quality of the data. While this degradation would not be directly shown by QC checks until the next required series of analytical QC analyses, a thorough review of the ongoing data acquisition can yield indicators of instrument performance.

C. Criteria

There are no specific criteria for system performance. Professional judgment should be applied to assess the system performance.

D. Evaluation

1. Abrupt discrete shifts in the chromatogram baseline may indicate a change in the instrument's sensitivity or the baseline setting. A baseline "shift" could indicate a decrease in sensitivity in the instrument or an increase in the instrument zero, possibly causing target compounds, at or near the detection limit, to miss detection. A baseline "rise" could indicate problems such as a change in the instrument zero, a system leak, or degradation of the column.

2. Poor chromatographic performance affects both qualitative and quantitative results. Indications of substandard performance include:

   a. High background levels or shifts in absolute retention times for calibration standards.

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b. Excessive baseline rise.

c. Extraneous peaks.

d. Loss of resolution.

e. Peak tailing or peak splitting that may result in inaccurate quantitation.

E. Action

Professional judgment must be used to qualify the data if it is determined that system performance has degraded during sample analysis.

XIV. OVERALL ASSESSMENT OF DATA

A. Review Items

Entire data package, data review results, QAPP and Sampling and Analysis Plan

B. Objective

The overall assessment of a data package is a brief narrative in which the data reviewer expresses concerns and comments on the quality and, if possible, the usability of the data.

C. Criteria

Assess the overall quality of the data.

Review the available materials to assess the overall quality of the data, keeping in mind the additive nature of analytical problems.

D. Evaluation

1. Evaluate any technical problems which have not been previously addressed.

2. If appropriate information is available, the reviewer may assess the usability of the data to assist the client in avoiding inappropriate use of the data. Review all available information, including the QAPP, Sampling and Analysis Plan, and communications with the client, that concerns the intended use and desired quality of these data.

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E. Action

1. Use professional judgment to determine if there is any need to qualify data which were not qualified based on the QC previously discussed.

2. Prepare a fully-documented quality assurance review which provides the client with an indication of the analytical limitations of the data. If sufficient information on the intended use and required quality of the data are available, the reviewer should include his assessment of the usability of the data within the given context.

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XV. AUTHORITY

This data validation SOP for the analysis for halogenated and aromatic volatile organic compounds has been prepared by Environmental Standards, Inc. This SOP represents internal control copy _____ issued to _____ and is not to be photocopied or used by any other entity except Environmental Standards, Inc. without expressed written permission.

SOP approved by:

_____ Date: _____
Rock J. Vitale, CPC
Technical Director of Chemistry/Principal

Control Copy No.: _____

Received by: _____

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STANDARD OPERATING PROCEDURES FOR DATA VALIDATION OF HARDNESS AS $CaCO_3$ (METHOD 130.1)

I. METHOD SUMMARY

This method is for the analysis of hardness in aqueous samples. The magnesium EDTA exchanges magnesium on an equivalent basis for any calcium and/or other cations to form a more stable EDTA chelate than magnesium. The free magnesium (from both the original sample and the EDTA complex which was released to form other EDTA chelates) reacts with calmagite at a pH of 10 to give a red-violet complex. Thus, by measuring only magnesium concentration in the final reaction stream, an accurate measurement of total hardness is possible. No significant interferences are known for this method.

II. HOLDING TIMES*

A. Review Items

Form I (or equivalent), Chain-of-Custody Forms, raw data and Case Narrative

B. Objective

The objective is to ascertain the validity of results based on the holding time of the sample from the time of collection to the time of analysis.

C. Criteria

Technical requirements for sample holding times are based on the project-specific QAPP. Samples must be cooled (to 4°C ± 2°C and acidified to pH <2 with nitric acid) for all water samples. The maximum holding time is six months from the date of sample collection to analysis when samples are properly preserved.

D. Evaluation

Verify that the samples were analyzed within 6 months from the date of sample collection specified on the Chain-of-Custody.

* **See Section XV. for authority and application of this SOP.**

E. Action

1. If the analysis of aqueous samples was performed after the 6 month holding time but within 9 months of collection, all samples results should be considered estimated ("J"). "Not-detected" results should be flagged "UJ".

2. If the analysis of the aqueous samples was performed more than nine months past the date of sample collection. The analysis should be considered unreliable and all results should be flagged "R".

3. Note the holding time exceedances in the QA report.

III. INITIAL CALIBRATION

A. Review Items

Calibration summary forms and raw data.

B. Objective

Compliance requirements for satisfactory instrument calibration are established to ensure that the instrument is capable of producing acceptable qualitative and quantitative data for target compounds.

C. Criteria

The method specifies that the initial calibration shall be performed with nine standards ranging in concentration from [illegible] mg $CaCO_3$/L to 400 mg $CaCO_3$/L. However, the method does not specify the frequency of the generation of the initial calibrations or what criteria is used to determine the acceptability of the initial calibration curve. Refer to the QAPP for project-specific requirements. Without other guidance, the following shall be used to assess data quality.

1. The laboratory shall use a ten-point calibration (nine standards and a reagent blank) for the generation of an initial calibration curve.

2. The correlation coefficient for the calibration curve shall be 0.995 or greater. Otherwise, the laboratory shall terminate the analysis, prepare new standards and recalibrate the instrument. All samples associated with an unacceptable initial calibration shall be reanalyzed.

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3. All samples shall be analyzed within 8 hours of the generation of the initial calibration curve/ Samples analyzed more than 8 hours after the generation of the initial calibration curve shall be reanalyzed.

D. Evaluation

1. Verify that a ten-point calibration for instrument standardization was performed.

2. Verify that the correlation coefficient for the initial calibration is 0.995 or greater.

3. Verify that all samples were analyzed within 8 hours of the generation of the initial calibration curve.

4. Verify that all information reported on the initial calibration quality control summary form is correct as reported from the raw data.

E. Action

1. Any missing items, inconsistencies or errors must be resolved by the laboratory.

2. If the laboratory used less than nine standards and a blank for the generation of the initial calibration curve, note this in the quality assurance review. Qualification of the data based on this issue is not necessarily required.

3. If the correlation coefficient for an initial calibration is less than 0.995 and the laboratory did not reprepare the standards and reanalyze the associated samples, note this in the quality assurance review. In addition, flag all positive results as estimated ("J"). Qualification of the "not-detected" results is not necessarily required based on this issue.

4. If samples were analyzed outside the 8-hour time limit from the generation of the calibration curve, note this deficiency in the quality assurance review. Qualification of the sample results is not necessarily required based solely on this issue.

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IV. CONTINUING CALIBRATIONS

A. Review Items

Continuing calibration summary forms and raw data.

B. Objective

The purpose of the continuing calibration analyses is to demonstrate instrument stability during the analysis of samples. Instrument drift or shift may affect the ability of the analysis to produce accurate sample results.

C. Criteria

The method does not specify criteria regarding the frequency and acceptability criteria for the continuing calibration analyses. Refer to the QAPP for project-specific requirements for continuing calibrations. Without other guidance, the following criteria shall be used to assess data quality.

1. The continuing calibration analysis shall be perfumed with a standard near the mid-range of the initial calibration curve.

2. The continuing calibration analysis shall be performed before and after all samples have been analyzed and after every 10 samples.

3. The continuing calibration shall display recoveries within 85-115%. Otherwise, the laboratory shall terminate the analysis, recalibrate the instrument, and reanalyze all samples analyzed since the last acceptable continuing calibration data.

D. Evaluation

1. Verify that all information reported on the continuing calibration summary form is correct as reported from the raw data.

2. Verify that the concentration of $CaCO_3$ in the continuing calibration standard is near the mid-range of the initial calibration standard.

3. Verify that the continuing calibration was performed at the beginning and end of the sample analysis and after every 10 samples.

4. Verify that the recoveries for all continuing calibration analyses were within 85-115%. and that all samples associated with an unacceptable continuing calibration analysis were reanalyzed (after the instrument was recalibrated).

E. Action

1. Any missing items, inconsistencies, or errors must be resolved by the laboratory.

2. If the concentration of the continuing calibration standards was not near the mid-range of the initial calibration, include a statement to this effect in the quality assurance report. Data is not necessarily qualified based solely on this issue.

3. If the continuing calibration was not performed at the specified frequency, include a statement to this effect in the quality assurance review. Qualification of the sample results is not necessarily required based solely on this issue.

4. If the laboratory reported a recovery outside the 85-115% acceptance range and did not recalibrate the instrument and reanalyze the associated samples, include a statement to this effect in the quality assurance report. In addition, data shall be qualified as follows:

   a. If the reported recovery is less than 85% but greater than 50%, flag all positive results in the associated samples as estimated ("UJ") and the "not-detected" results "UJ".

   b. If the reported recovery for a continuing calibration standard is less than 50%, the analysis for hardness in the samples should be considered unreliable and the sample results in all associated samples should be flagged "R".

   c. If the reported recovery for a continuing calibration standard is greater than 115% but less than 150%, flag all positive results in the associated samples as estimated ("J"). Qualification of "not-detected" result in the associated samples is not necessarily required based on this issue alone.

   d. If the recovery for a continuing calibration standard exceeds 150%, the analysis should be considered unreliable and the positive results for hardness in all associated samples should be flagged "R". Qualification of "not-detected" results is not necessarily required based solely on this issue.

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V. METHOD BLANKS CALIBRATION AND FIELD BLANKS

A. Review Items

Quality control summary forms, analytical results forms, and raw data.

B. Objective

The assessment of blank analysis results determines the existence and magnitude of contamination problems. The criteria for evaluation of blanks apply to any blank associated with the samples. If problems with any blank exist, all associated data must be carefully evaluated to determine whether or not there is an inherent variability in the data, or if the problem is an isolated occurrence not affecting other data.

C. Criteria

The method does not give guidance as to the frequency or acceptability for the method or calibration blanks. See the QAPP for project-specific criteria for these blanks and for the field, rinse, or equipment blanks. Without guidance from the QAPP, the following criteria shall be used to assess data quality.

1. A method blank (reagent water carried through all sample digestion and analysis steps) shall be prepared at a frequency of one per twenty samples or with every batch of samples, digested, whichever is more frequent. Note that a method blank is not necessary if the samples are not digested prior to analysis. Only wastewater and heavily contaminated aqueous samples should require digestion prior to analysis. Drinking waters do not need to be digested.

2. The method blank shall not display positive results for the analyte greater than the method detection limit (MDL). If the method blank displays a positive result greater than the MDL, the laboratory shall redigest and reanalyze all associated samples.

3. A calibration blank shall be analyzed immediately after every continuing calibration standard analysis.

4. The calibration blanks shall not display positive results for the analytes at levels greater than the MDL. If a calibration blank displays a positive result greater than the MDL, the laboratory shall terminate the analysis, recalibrate the instrument, and reanalyze all samples analyzed since the last compliant calibration blank.

5. A field, rinse, and/or equipment blank shall be collected at a frequency of one per twenty field samples or per the frequency stated in the project-specific QAPP.

6. A field, rinse, and/or equipment blank shall not display levels of the analytes at levels greater than the MDL.

7. The laboratory shall not blank subtract any positive result reported for the analysis.

D. Evaluation

1. Verify the reported results against the raw data to determine consistency and to determine if these blanks have acceptable calibrations.

2. Verify that every sample within the data set has an associated method blank (if sample digestion was necessary).

3. Verify that each method blank does not contain the analyte in excess of the method detection limit.

4. Verify there is a field and/or rinse blank for every data set of 20 samples or less, or per the frequency stated in the QAPP.

5. Verify that the field, equipment, and/or rinse blanks do not contain the analyte above the method detection limit.

6. Verify that the laboratory did not blank-subtract the positive sample results.

E. Action

1. Any missing items, inconsistencies or errors must be resolved by the laboratory

2. If the laboratory has utilized blank subtraction, the laboratory must resubmit the data unsubtracted.

3. If a field and/or rinse blank is not present, note this in the QA report.

4. If the analyte is present in any blank above the method detection limit, the following apply:

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a. If an analyte is detected in any sample within 5 times the reported in the blank, the result is qualitatively questionable and is qualified "U" on the target summary table.

b. If the concentration of the analyte in any sample is greater than 5 times the blank result, do not flag results, but note the level in the blank in the QA report.

5. If the method blank displayed a positive result for an analyte at a level greater than the MDL and the associated samples were not redigested and reanalyzed, include a statement in the quality assurance review to this effect.

6. If the calibration blank displayed a positive result greater than the MDL and the laboratory did not recalibrate the instrument and reanalyze all associated samples, include a statement to this effect in the quality assurance review.

V. MATRIX SPIKE/MATRIX SPIKE DUPLICATES, BLANK SPIKES AND LABORATORY CONTROL SAMPLES

A. Review Items

Quality control summary forms, analytical results summaries, and raw data.

B. Objective

Data for matrix spikes (MS)/matrix spike duplicates (MSD) are generated to determine long-term accuracy and precision of the analytical method on various matrices and to demonstrate acceptable compound recovery by the laboratory at the time of sample analysis. The data for blank spikes (BS) and laboratory control samples (LCS) are generated to determine analytical accuracy. The results of blank spikes and LCS are used to assess accuracy of the entire sample batch.

C. Criteria

The method does not provide guidance as to the frequency or recovery criteria for the BS and LCS analyses. Refer to the QAPP for project-specific requirements for these analyses and for the MS/MSD analyses. Without project-specific criteria, the data shall be evaluated based on the following criteria.

1. An MS/MSD shall be digested with every twenty samples or with every batch of samples digested, whichever is more frequent. A designated field, rinse, or equipment blank shall <u>not</u> be used for the MS/MSD analysis.

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2. The recovery for the MS/MSD pair shall be 75-125%, and the relative percent difference between the results for the MS/MSD analysis shall not exceed 20%.

3. A BS analysis shall be performed with every batch of samples analyzed or for every 20 samples, whichever is more frequent.

4. The BS analysis shall display a recovery within 85-115%. IF the BS analysis displays a recovery outside of this criteria, the laboratory shall recalibrate the instrument and reanalyze all samples associated with the BS analysis.

5. A LCS shall be digested for every 20 samples or with every batch of samples digested, whichever is more frequent.

6. The LCS shall display a recovery of 85-115%. If the LCS displays a recovery outside this criterion, the laboratory shall redigest and reanalyze all samples associated with the LCS.

D. Evaluation

1. Verify that a MS/MSD pair was performed at a frequency 1 in 20 samples or with every batch of samples digested, whichever is more frequent. Also verify that a BS or LCS was analyzed with every 20 samples or with every batch of samples analyzed, whichever is more frequent.

2. Verify that there is consistency between the raw data and the recoveries reported.

3. Verify that the MS/MSD recoveries were within the range of 75-115% and that the BS or LCS recoveries were within the range of 80-120%.

4. Verify that the MS/MSD analysis was not performed on a designated field, equipment, or rinse blank.

E. Action

1. Any inconsistencies/errors must be resolved by the laboratory.

2. If an MS/MSD was not performed at the required frequency, include a statement to this effect in the quality assurance review.

3. If the MS/MSD was performed on a designated field or rinse blank, note the deficiency in the QA report.

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4. If the recoveries are outside criteria, the following apply:

Matrix Spikes/Matrix Spike Duplicates

a. %R < 75% but > 40%, flag positive results "J" and flag "not-detected" results "UJ".
b. %R < 40%, flag positive results "J" and "not-detected" results as unreliable ("R").
c. %R > 125% but < 150% , flag positive results "J". Note that "not-detected" results do not necessarily require qualification.
d. %R > 150%, flag positive results as unreliable ("R"). Note that "not-detected" results do not necessarily require qualification.

Blank Spikes and LCS

a. %R < 85% but > 50%, flag positive results "J" and flag "not-detected" results "UJ".
b. %R < 50%, flag positive results "J" and "not-detected" results as unreliable ("R").
c. %R > 115% but < 150%, flag positive results "J". Qualification of "not-detected" results is not necessarily warranted in this instance.
d. %R > 150%, flag all positive results as unreliable ("R"). Qualification of "not-detected" results is not necessarily warranted in this instance.

In all situations above, the validation report must indicate the direction and severity of the bias.

5. If the relative percent difference for the results from the MS/MSD analysis exceeds 20%, flag all positive results in the associated samples as estimated ("J"). Qualification of "not-detected" results in the samples is not necessary.

6. If the BS or LCS analysis displays an unacceptable recovery for an analyte and the laboratory did not reprepare and reanalyze the samples, note the deficiency in the quality assurance report.

VII. LABORATORY DUPLICATES

A. Review Items

Raw data, analysis summary forms, and the laboratory duplicate analysis summary form.

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B. Objective

The laboratory duplicate analysis is used to provide an indication of laboratory performance in terms of analytical precision. Several factors, including sample homogeneity (to a minimal extent) and laboratory performance, may effect the overall precision demonstrated by the laboratory.

C. Criteria

The methods do not give a frequency or relative percent difference (RPD) criteria for the laboratory duplicate analysis. Refer to the QAPP for project-specific criteria. For data validation purposes, the RPD should be less than 20%. If both results for the initial and laboratory duplicate analyses are > 5 times the MDL; or if one or both of the results from the initial or laboratory duplicate analyze is less than 5 times the MDL, the two results should be within ± 2×MDL.

D. Evaluation

1. Verify that a laboratory duplicate was performed at a frequency specified in the QAPP.

2. Verify that there is consistency between the raw data and the RPDs reported.

3 Verify that the RPDs are within 20%. If both results for the initial and laboratory duplicate analyses are > 5 times the MDL; if one or both of the results from the initial or laboratory duplicate analyses is less than 5 times the MDL, the two results should be within ± 2×MDL.

4. Verify that laboratory duplicates were not performed on field, equipment, or rinse blanks.

E. Action

1. Any inconsistencies/errors must be resolved by the laboratory.

2. If the laboratory duplicate was not performed, note the deficiency in the QA report.

3. If the laboratory duplicate was performed on a designated field, equipment, or rinse blank, note the deficiency in the QA report.

4. Use the following guidelines to qualify data based on the laboratory duplicate analysis results.

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a. If the initial and laboratory duplicate analysis results are greater than 5× MDL, and the RPD between the results is greater than 20%, flag all positive results for sulfate in the associated samples as estimated ("J"). Qualification of "not-detected" results is not required due to high RPDs in the laboratory duplicate analysis.

b. If one or both of the initial or laboratory duplicate analysis results is less than 5× MDL, and the difference between the two results exceeds 2× MDL, then flag all positive results for sulfate in the associated samples as estimated ("J"). Qualification of "not-detected" results for sulfate in the samples is not warranted due to the large difference between the two results.

IX. FIELD DUPLICATES

A. Review Items

Form I VOAs, chromatograms and quantitation reports.

B. Objective

Field duplicate samples may be taken and analyzed as an indication of overall precision. These analyses measure both field and laboratory precision; therefore, the results may have more variability than laboratory duplicates which measure only laboratory performance. It is also expected that soil duplicate results will have a greater variance than water matrices due to difficulties associated with collecting identical field samples.

C. Criteria

There are no specific review criteria for field duplicate analyses comparability; however, validation criteria are specified below. Refer to QAPP for project-specific requirements concerning frequency of collection of field duplicates and the precision necessary for the data quality objectives. The RPD should be less than 25% if both results for the initial and field duplicate analyses are greater than five times the method detection limit; if one or both of the results from the initial and/or field duplicate analysis are less than five times the MDL, the two results should agree within ±2× MDL.

D. Evaluation

Samples which are field duplicates should be identified. Check the Chain-of-Custody Records or contact the client for field duplicate information. The reviewer should compare the results reported for each sample and duplicate and calculate the relative percent difference (RPD) for the field duplicate pair.

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E. Action

Positive results for a target compound should be flagged "J" in the sample and its duplicate if the following criteria are not met.

1. A control limit of ±25% for aqueous samples for the RPD shall if both the initial sample and field duplicate sample display results greater than 5× the MDL.

2. A control limit of ±2× the MDL shall be used for all samples if either one or both of the initial and field duplicate sample results were less than 5× the MDL.

VIII. COMPOUND QUANTITATION AND REPORTED QUANTITATION LIMITS

A. Review Items

Raw data, analytical results forms, and SDG case narrative.

B. Objective

The objective is to ensure that the reported quantitative results and quantitation limits (QLs) are accurate. Transcription errors are often a problem with inorganic analyses in which direct instrument printouts are not possible. Therefore, a close scrutiny of the analysis logs and reported results is necessary.

C. Criteria

All positive results must be quantitated correctly and within the calibration range of the instrument. The laboratory must provide all raw data to allow for all positive results to be recalculated and all "not-detected: results to be verified.

D. Evaluation

1. Verify all required data is present. Verify all laboratory calculations are present for all positive sample results and QC samples results.

2. Recalculate 100% of the positive sample results.

3. Verify that all positive results were quantitated within the calibrated range.

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E. Action

If there are any discrepancies found, the laboratory may be contacted to obtain additional information that could resolve differences. If a discrepancy remains unresolved, the reviewer may determine that qualification of the data is warranted.

1. Any data that is incorrect and/or missing (i.e., sample calculations) must be resolved/submitted by the laboratory.

2. If a positive result for an analyte in a sample was quantitated from an instrument level greater than the calibration range of the instrument, flag the positive result as estimated ("J") and include a deficiency in the quality assurance report.

XI. OVERALL ASSESSMENT OF DATA

A. Review Items

Entire data package, data review results, and the project-specific QAPP and Sampling and Analysis Plan

B. Objective

The overall assessment of a data package is a brief narrative in which the data reviewer expresses concerns and comments on the quality and, if possible, the usability of the data.

C. Criteria

Assess the overall quality of the data.

Review all available materials to assess the overall quality of the data, keeping in mind the additive nature of analytical problems.

D. Evaluation

1. Evaluate any technical problems which have not been previously addressed.

2. If appropriate information is available, the reviewer may assess the usability of the data to assist the data user in avoiding inappropriate use of the data. Review all available information, including the QAPP, Sampling and Analysis Plan and any communications with the client that concern the intended use and desired quality of these data.

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E. Action

1. Use professional judgment to determine if there is any need to qualify data which were not qualified based on the QC previously discussed.

2. Prepare a fully documented quality assurance review for the client which provides an indication of the analytical limitations of the data. If sufficient information on the intended use and required quality of the data are available, the reviewer should include his assessment of the usability of the data within the given context.

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XII. AUTHORITY

This data validation SOP for the analysis for hardness as $CaCO_3$ has been prepared by Environmental Standards, Inc. This SOP represents internal control copy _____ issued to _____ and is not to be photocopied or used by any other entity except Environmental Standards, Inc. without expressed written permission.

SOP approved by:

_____ Date: _____
Rock J. Vitale
Quality Assurance Specialist/Principal

Control Copy No.: _____

Received by: _____

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APPENDIX B

ENVIRONMENTAL STANDARDS INC.

PERSONNEL PROFILES

KATHLEEN A. BLAINE

Quality Assurance Specialist/Principal

FIELDS OF COMPETENCE

- Analytical services design.
- Litigation support.
- Documentation for litigation support.
- Data validation for analytical and environmental chemistry.
- Multi-media fate and transport mechanisms of pollutants.
- Petroleum-related litigation support and technical oversight.
- RFP preparation.
- Analytical data adequacy determination for RI/FS, RCRA, RFIs, RCRA Permit B, and delisting studies.
- Sampling protocols.
- Technical liaison among laboratories, industries, and consultants.
- Theoretical and practical knowledge of all facets of quantitative analysis for organic and inorganic pollutants by US EPA methodologies.
- Laboratory auditing.
- Third-party reviews of Quality Assurance Project Plans.

CREDENTIALS

B.S., Chemistry, Butler University, Indiana, 1984.

Wright State University, Ohio. Graduate Chemistry Course Work.

PROFESSIONAL AFFILIATIONS

US EPA Certified Drinking Water Laboratory Certification Officer - Chemistry and Microbiology
American Chemical Society
American Society of Testing and Materials
(Subcommittees D18.21-D18.99)
AOAC International
American Association for Laboratory Accreditation (A2LA)

SUMMARY OF EXPERIENCE

Ms. Blaine has over thirteen years of analytical/quality assurance experience. Specifically, she has four years of analytical experience performing analyses for organic and inorganic contaminants in a variety of media by instrumental and classical methods, including research and development of dioxin and furan soil and water partitioning. As a Quality Assurance Specialist, Ms. Blaine performs complex data validations for all media and project types. Ms. Blaine is a recognized expert in the fields of organic and inorganic data validation (including specialty analyses), laboratory auditing; preparation of third-party review of quality assurance project plans (QAPjPs) for remedial investigations/feasibility studies (RI/FS), Resource Conservation and Recovery Act (RCRA), Comprehensive Environmental Response, Conservation, and Liability Act (CERCLA) and remedial actions; design of quality assurance programs; and agency negotiations.

Prior to joining Environmental Standards, Ms. Blaine was the Divisional Laboratory Administrator and Quality Assurance Manager for a large environmental consulting firm with ten offices nationwide. She designed and implemented a quality assurance and data validation program for all RI/FSs, site inspections, and RCRA closures. Her responsibilities included the preparation of QAPjPs for Superfund studies in US EPA Regions II, IV, V, VII, VIII, and X. She also trained and managed a staff of four data reviewers. In addition, Ms. Blaine has been one of the top ranked A2LA Environmental Laboratory assessors for the past nine years.

Prior to that position, Ms. Blaine had two years of experience as an organic and inorganic laboratory supervisor with a primary US EPA Superfund contractor. She provided quality assurance reviews for all analytical data generated within the laboratory, based upon rigorous examination of gas chromatography (GC), GC/mass spectroscopy (MS) (high and low resolution), graphite furnace atomic absorption (GFAA), and inductively coupled plasma (ICP) data

KEY PROJECTS

- Performed data validation for more than 600 RI/FSs, RFIs, CERCLA RFIs, remedial actions, and for routine monitoring projects on data generated by more than 40 laboratories on projects throughout the United States.

- Prepared QAPjPs, which included formulation of data quality objectives (DQOs), for more than ten privately funded RI/FS, RFIs, and remedial actions (e.g., drum removals) for submission to federal and state regulatory agencies. Also, performed third-party review and comment on QAPjPs prepared by other entities for a significant number of RI/FSs and RFIs prior to submission of the documents to the lead regulatory agency.

- At the request of Fortune 500 companies, A2LA, and, in some instances, laboratories themselves, performed comprehensive laboratory audits on over 150 laboratories nationwide in the areas of organic analyses, inorganic analyses, classical parameters, and specialty analyses. Provided critical comments, recommendations, and performance evaluation (PE) reports.

- Prepared a significant number of comprehensive Requests for Proposals (RFPs) for analytical services for a wide variety of large short- and long-term environmental investigations. Evaluated laboratory proposals, provided recommendations for award, and participated in contract negotiations.

- Trained and supervised a staff of four quality assurance personnel between three environmental consulting offices. In addition, conducted numerous training seminars on environmental quality assurance for environmental project managers.

- Prepared laboratory bid specifications for several Fortune 500 companies as part of a laboratory selection process.

- Reviewed numerous site specific data packages in order to provide technical advice in association with potential litigation.

PUBLICATION

Adams, W. and K. A. Blaine. "Dioxin Soil-Water Partitioning Coefficients." Chemosphere (October 1984).

JILL B. HENES, Ph.D.

Quality Assurance Specialist/Principal

FIELDS OF COMPETENCE

- Utilizing theoretical and practical knowledge of all facets of quantitative analysis for organic and inorganic pollutants by US EPA methodologies.
- Determining the adequacy of analytical data generated to support RI/FS(s), RCRA RFI(s), RCRA Permit B(s), delisting studies, etc. Methods include those for US EPA Contract Laboratory Program (CLP) protocols, SW 846 Methods, Methods for the Chemical Analysis of Water and Wastes, the US EPA Series 200 and 600 methods, and all dioxin/furan methods (8280, 8290, Modified Method 5 and related methods, 1613A, 613 and CLP SOW DFLM01.1).
- Performing rigorous laboratory audits to determine the adequacy of laboratory operations.
- Preparing or performing third-party reviews of Quality Assurance Project Plans (QAPjPs).
- Serving as a technical liaison between laboratories, industries, and consultants.
- Designing specific requirements and specifications for analytical services and sampling protocols, providing data validation and documentation for litigation, and preparing project-specific Requests for Proposals (RFPs).
- Providing litigation support and dispute resolution; expert witness.
- Training and managing data review staff.

CREDENTIALS

M.B.A., Duke University, Durham, North Carolina, 1986.

Ph.D., Chemistry, Case Western Reserve University, Cleveland, Ohio, 1976.

- Received DuPont Award for Excellence for Undergraduate Teaching, 1975.

M.S., Chemistry, Case Western Reserve University, Cleveland, Ohio, 1974.

B.S., Chemistry, University of Vermont, Burlington, Vermont, 1972.

- Received Brown Award for Most Outstanding Undergraduate Chemistry Student (1972)
- National Science Foundation Scholarship Grant for Undergraduate Research (1971).

PROFESSIONAL AFFILIATIONS

Interagency Steering Committee for Quality Assurance for Environmental Measurements
American Chemical Society
American Society of Agronomy
Crop Science Society of America
Soil Science Society of America

SUMMARY OF EXPERIENCE

Dr. Henes has eighteen years of analytical/quality assurance experience. She has twelve years of experience performing analyses for organic and inorganic contaminants, managing GC and Dioxin Programs, managing large projects for industrial clients, and directing research and development activities. In addition, she has four years of experience as the Managing Principal of

Environmental Standards-West, Inc. in Davis, California, where she directs the technical, business development, and managerial aspects of the operations. Dr. Henes is a recognized expert in the fields of organic and inorganic quality assurance and dioxin/furan analysis.

Dr. Henes has conceived, designed, and/or implemented comprehensive quality assurance programs for Fortune 500 companies, environmental laboratories, petroleum condition monitoring laboratories, and environmental remediation and environmental engineering companies. This included preparing or reviewing Quality Assurance Plans and SOPs, performing audits, submitting and evaluating blind performance evaluation samples, evaluating quality systems, method detection limit studies, and laboratory-generated analytical data, problem resolution, and general consulting.

In addition, Dr. Henes has acted as an expert witness providing analytical chemistry support for litigation involving a Fortune 500 chemical company and a major environmental engineering company. She has conducted research and/or provided research papers on topics in environmental/analytical chemistry including laboratory contamination, analytical method modifications, fate and transport of aromatic hydrocarbons in groundwater, and iron bacteria.

Prior to 1992, Dr. Henes was employed by several major CLP laboratories in a variety of positions. As the Quality Assurance Director of one CLP laboratory, she was responsible for conceiving and implementing a comprehensive quality assurance program. This included rewriting the QAPP, writing and/or reviewing SOPs, and implementing numerous quality systems within the laboratory.

Before assuming the QA Director's responsibilities, Dr. Henes was a Technical Services Director with responsibilities including project management for key industrial accounts, directing research and development for analytical methodology, and managing several functional areas within the laboratory. The projects managed involved groundwater monitoring, remedial investigation/feasibility studies, site and waste characterization, and bioremediation.

During this period of time, Dr. Henes served on the US EPA Dioxin Work Group and assisted in writing the current CLP protocols for 2,3,7,8-TCDD and PCDD/PCDF analyses, and served on the US EPA Fast Turnaround Method Work Group, and provided input and critical review of methods used for the current protocols.

At another CLP laboratory, Dr. Henes was responsible for the GC and Dioxin Programs. She directed the development of the analytical, extraction, and clean-up techniques used for sample preparation and analysis of dioxin and furan compounds. She served as US EPA dioxin contact to US EPA's Sample Management Office, US EPA regional offices, and US EPA headquarters. She attended briefings and workgroup meetings and assisted in writing the 1986 CLP dioxin protocol, Method 8280 (1986), and the CLP SOW DFLM01.1. She also directed work on method development projects and method validation projects for the US EPA Office of Solid Waste SW-846 Methods 8080, 8140, 8150, and 8280.

Dr. Henes' first position in the environmental industry involved the start-up and subsequent managing of a small on-site laboratory for monitoring 117 groundwater wells at a Fortune 100 company. The laboratory is now a multi-facility/multi-million dollar operation.

KEY PROJECTS

- Twenty-six years of experience in chemistry including sixteen years of experience in environmental analytical chemistry.
- Twelve years of experience at two major US EPA contracting laboratories and experience working with various analytical protocols, including SW 846 Methods, US EPA-CLP SOWs, Federal Register 500 and 600 series organics methods, inorganic and classical chemistry procedures found in *Standard Methods and in the Chemical Analysis of Water and Wastewater Manual*, ASTM Methods, and dioxin/furan protocols.
- Eleven years of experience managing laboratory dioxin/furan programs.

- Participated in two environmental laboratory startups.

- Laboratory Director for two major US EPA contracting laboratories.

- Five years of experience as a client manager for private industry, US EPA-CLP, Navy, Army Corps of Engineers, and Hazwrap projects. Project manager for dozens of environmental engineering/consulting accounts. Responsibilities included scheduling and tracking analyses, reviewing data, writing accompanying case narratives, and finalizing analytical reports.

- Performed analytical data validation for numerous site investigations to determine analytical data outliers and data quality/usability. Data reviewed included those for US EPA Contract Laboratory Program (CLP) protocols, SW 846 Methods, Methods for the Chemical Analysis of Water and Wastes, the US EPA Series 200 and 600 methods, ASTM Methods, and various dioxin/furan methods.

- Member of US EPA work-group committees that have been instrumental in developing and writing the Fast-Turnaround Organic Analysis and the PCDD/PCDF Analysis Statements of Work.

- Written and/or reviewed Quality Assurance Project Plans for several environmental laboratories and engineering consulting companies.

- Conducted on-site system audits of many industrial and contract environmental laboratories to identify deficiencies, provide critical comments, and make recommendations for improvement. The audits were based upon issues of good laboratory practices, laboratory quality assurance/quality control programs, and required analytical methods. Participated in preparation of audit responses to State and Federal Regulatory Agencies and the US Department of Justice.

- Created and implemented quality assurance programs for several laboratories, Fortune 500 companies, and environmental engineering and environmental remediation companies.

- Served as an expert witness providing testimony on chemistry and quality assurance.

PUBLICATIONS

Henes, J. B. and W. G. Kay (J.W. Conrad, editor). "Physics and Chemistry." The Environmental Science Deskbook. New York, NY. Clark Boardman Callaghan Publishers, 1996.

Henes, J. B., M. Briggs, S. G. Sligar, and J. S. Fruton. "Fluorescence Energy Transfer Studies on the Active Site of Papain." Proc. National Academy of Science 77 (1980)

Henes, J. B., J. A. Mattis, and J. S. Fruton. "Fluorescence Studies on the Interaction of Papain with Derivatives of Phenylalanylglycinal." Proc. National Academy of Science 76 (1979):1131.

Bodanszky, M., J. B. Henes, S. Natarajan, and R. L. Foltz. "Ring Formation in a Pentapeptide with Alternating L and D Residues: An Analogy to Cyclization in the Biosynthesis of Peptide Antibiotics." Journal of Antibiotics 30 (1977):856.

Mattis, J. A., J. B. Henes, and J. S. Fruton. "Interaction of Papain with Derivatives of Phenylalanylglycinal." Journal of Biol. Chem. 252 (1977):6776.

Bodanszky, M., J. B. Henes, A. E. Yiotakis, and S. I. Said. "Synthesis and Pharmacological Properties of the N-Terminal Decapeptide of the Vasoactive Intestinal Peptide (VIP)." Journal of Medical Chemistry 20 (1977):1461.

Henes, J. B. Thesis: "Synthesis and Physical Studies of the Cyclic Pentapeptide Desthiomalformin." 1976.

Bodanszky, M., J. B. Henes, S. Natarajan, G. L. Stahl, and R. L. Foltz. "High Resolution Mass Spectra of Malformin and Related Cyclic Peptides." Journal of Antibiotics 29 (1976):549.

Bodanszky, M. and J. B. Henes. "Synthesis and Properties of the Cyclopentapeptide Desthionalformin." Bioorganic Chemistry 212 (1975).

Bodanszky, M., J. B. Henes, S. Natarajan, and G. L. Stahl. "Cyclic Pentapeptides Related to Malformin." Polymer Preprints 16 (1975):133.

PRESENTATION

Henes, J. B. and W. G. Kay. "Determination of the Validity of OCDD Results at an Industrial Site." SUPERFUND XV. Washington, DC, 29 November-1 December 1994.

ENVIRONMENTAL STANDARDS

MEG A. CLARK

Senior Quality Assurance Chemist II

FIELDS OF COMPETENCE

- Interfacing between laboratories, industries, and consultants.
- Performing analytical data validation to determine analytical data outliers and quality/usability.
- Performing rigorous laboratory audits to determine the adequacy of laboratory operations.
- Preparing and performing third-party reviews of Quality Assurance Project Plans (QAPjPs).
- Preparing and reviewing project-specific analytical methods, analytical deliverables, data validation, and laboratory auditing Standard Operating Procedures (SOPs).
- Preparing project-specific Request for Proposals (RFPs) for analytical services.
- Providing technical and QA/QC oversight for various industrial clients.
- Training and managing data review staff.

CREDENTIALS

M.S., Organic Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania, January 1991.

B.A., Chemistry, Gettysburg College, Gettysburg, Pennsylvania, May 1989.

Radiological, Inorganic, Volatile/Semivolatile and Pesticide/PCB Data Verification and Validation Training, Lockheed Martin Energy Systems, Inc. Environmental Restoration Data Quality Program, April 1996.

SUMMARY OF EXPERIENCE

Ms. Clark has seven years of analytical/quality assurance experience. As a senior quality assurance chemist, Ms. Clark manages various projects and staff within the Valley Forge, Pennsylvania, office. Ms. Clark is knowledgeable in the fields of organic and inorganic data validation, laboratory auditing, preparing and third-party reviewing SOPs and QAPjPs, preparing analytical laboratory RFPs and reviewing laboratory proposals, and the training of quality assurance chemists.

Prior to joining Environmental Standards, Ms. Clark worked as a research chemist and a graduate teaching assistant at the University of Pennsylvania. Ms. Clark's research efforts were directed toward the total synthesis of detoxin D_1 which allowed her to develop skills in spectroscopic and separation techniques (^{1}H-NMR, IR, flash column chromatography). As a teaching assistant, Ms. Clark was responsible for overseeing organic laboratory experiments in a classroom environment and grading laboratory experiment reports and examinations. Ms. Clark also performed undergraduate research which involved the synthesis of novel facially-capping ligands in order to prepare models for the binuclear iron Purple Acid Phosphatase. As part of this research, Ms. Clark developed skills in spectroscopic techniques (^{1}H- and ^{13}C-NMR, FT-IR, GC/MS).

KEY PROJECTS

- Performed analytical data validation for numerous site investigations to determine analytical data outliers and data quality/usability. Data reviewed include those for US EPA Contract Laboratory Program (CLP) protocols, SW-846 Methods, Methods for the Chemical Analysis of Water and Wastes, and the US EPA Series 200, 500, and 600 methods.

KEY PROJECTS (Cont.)

- As part of data validation support for a site investigation, observed unusually high levels of interferences in standard ICP metals analyses. Advised the client to have the laboratory confirm some of the metal results by ICP/MS. The ICP/MS methodology was chosen for the confirmational analysis because it is not subject to the same interferences, as the ICP analysis is qualitatively very specific and generally more sensitive than the standard ICP analysis. The ICP/MS results generally supported the ICP results with a few notable exceptions. A concentration range for these exceptions was determined based on the two analyses.

- Data validation project manager for many major US EPA Region I, Region II, Region III, Region V, and NYSDEC site investigations. Project management duties include logging in and tracking data, providing technical assistance in data validation problems, reviewing quality assurance reports, tracking budgets for data package review, and providing technical assistance to clients. At times, project management has included advising laboratories on data deliverables prior to the investigation start, direct feedback to the laboratories to correct reporting errors and to improve on-going analytical work, and arranging for laboratory data deliverables to be generated after significant time lapses from when the analyses were performed. Project Management has also included providing advice to engineering contractors on data quality concerns. Provided recommendations for sample bottleware preservation, technical holding times, shipment and field quality control measures. Coordinated shipments of bottleware and environmental samples between the laboratory and the field and provided corrective action recommendations for any problems which arose.

- Managed several data validation projects for large New York State Superfund site investigations. Projects involved the full validation of data from over 1000 samples collected from the sites. Samples were contaminated with complex mixtures of Aroclors 1248, 1254, and/or 1260. Utilized in-house tools for PCB data validation so that a consistent approach to the qualitative identifications and quantitation of results could be used with all sample analyses. One project used a modification of a NYSDEC Superfund Method for the analysis for PCBs. Also advised the laboratory on improvements to the method for future analytical work for this project.

- Provided project management for an on-going data validation project for a drum disposal site. For this project, several analytical methods were required for each class of analytes due to the various levels of contamination at the site. Data examined included data for highly contaminated samples which caused many unique analytical problems. Provided significant chemistry consultation to the client regarding data validation, analytical, and database reporting issues.

- Assisted in project management and served as data validation task manager for an on-going quality assurance/quality control technical oversight project for large aircraft manufacturer. Prepared SOPs for laboratory audits, analytical work, data validation of analytical work, preparation of analytical data packages, and preparation of quality assurance reports for this extensive site investigation. In preparing the SOPs, coordination with several analytical laboratories, the data management contractor, and the client was essential. Subsequent data validation was performed for several phases of the investigation according to the requirements of data validation SOPs which included a data quality assessment and a compliance evaluation based on the analytical SOPs. Extensive coordination with the data management contractor was required throughout the validation efforts in order to identify problems in the database and to update the database remotely.

- At the request of a client, reviewed data validation reports prepared by a competitor on herbicide and pesticide/PCB analytical data for a wetlands site investigation. Identified major qualitative and quantitative laboratory errors which were missed by the competitor. The qualitative errors had a major impact on the risk assessment for the site investigation. The discovery of the errors resulted in major changes by the laboratory in its approach to the analysis for pesticides/PCBs.

- Performed laboratory audits for several major companies to assess laboratory quality and reliability. As requested by the client, the audits evaluated laboratory personnel's use of good laboratory practices, laboratory quality control/quality assurance programs, and analytical methods.

- Performed audit of an on-site industrial laboratory with the primary function of providing analytical support for procedures involved in decommissioning electrical transformers and various other electrical equipment. The laboratory analyzed dielectric oil from the equipment in order to determine if (and at what concentration) PCBs were present based on US EPA guidelines. These analyses were used to categorize equipment for disposal. In addition, the facility collected and analyzed wipe samples from the surface area of scrap parts to ensure low levels of residual PCBs. Prepared audit report summarizing findings and key recommendations for the client to improve the qualitative and quantitative QA/QC for the analyses performed.

- Has prepared and third-party reviewed several project-specific QAPjPs, which included the participation in the formulation of project strategy and Data Quality Objectives (DQOs) for submission to federal and state regulatory agencies. Has addressed comments provided by agencies on QAPjP concerns. Has provided project-specific justification for project reporting limits which did not meet regulatory agency requirements. Has also reviewed and revised Sampling and Analysis Plans.

- Provided consultation on identifying analytical alternatives to potentially expensive state requirements for analytical work for a site investigation directed by the Virginia Department of Environmental Quality. The state was requiring the use of numerous analytical methods for the analysis of only a few classes of analytes. Developed a multi-tiered decision-tree approach which provided a dramatically less expensive alternative that met the data quality objectives of the project and that overlapped with some of the requirements of the coinciding RCRA facility investigation. Also modified the QAPjP for the RCRA facility investigation to include the alternative analytical approach.

- Prepared appendices for use in a corporate environmental contract laboratory program as a guideline for the use of the corporate environmental contract laboratory program: Laboratory Specifications Manual and Analytical Services and Quality Assurance Guidance Manual, specifically for waste characterization as it relates to hazardous waste management under the Resource Conservation and Recovery Act (RCRA).

- Prepared the RFP of analytical services for a monitoring program for a major company. The RFP addressed issues including budget, personnel, experience, instrumentation, and laboratory quality control/quality assurance programs. Reviewed proposals submitted by the laboratories in response to the RFP to determine the most qualified applicant. Reviewed and aided in re-writing the project-specific laboratory quality assurance project plan prepared by the contract laboratory.

- Performed a scientific evaluation of the results from the analyses of fly ash samples in an attempt to identify the possible sources of waste materials at a landfill. The evaluation included determining which analytes should be considered indigenous to the landfill, grouping these analytes based on chemical structure and industrial processes, and comparing the groupings and individual compounds to the manufacturing processes used by various local industries.

- Prepared and issued a one-page survey to the clients of a laboratory in order to evaluate the laboratory's performance in the opinion of their clients. The survey responses were compiled and evaluated in order to determine specific areas in which the laboratory could ultimately improve their services to their clients.

- Assisted a laboratory in the application process for certification in the Environmental Laboratory Accreditation Program in the State of California. Obtained and reviewed the application and provided laboratory with a detailed list of information required to complete the application process. Upon receipt of all necessary information from the laboratory, completed the application and provided final instruction to the laboratory.

PUBLICATION

Clark, M. A. and R. J. Vitale. "How to Assess Data Quality for Better Decisions." Clearwater. New York Water Environmental Association (NYWEA), Vol. 26, No. 2 (Summer 1996).

PRESENTATION/PAPER

Clark, M. A. and M. J. Piccone. "Regional Variations in the Evaluations of Analytical Data." SUPERFUND XV. Washington, DC, 29 November-1 December 1994

ENVIRONMENTAL
STANDARDS

ENVIRONMENTAL STANDARDS

MEG A. CLARK

Senior Quality Assurance Chemist II

FIELDS OF COMPETENCE

- Interfacing between laboratories, industries, and consultants.
- Performing analytical data validation to determine analytical data outliers and quality/usability.
- Performing rigorous laboratory audits to determine the adequacy of laboratory operations.
- Preparing and performing third-party reviews of Quality Assurance Project Plans (QAPjPs).
- Preparing and reviewing project-specific analytical methods, analytical deliverables, data validation, and laboratory auditing Standard Operating Procedures (SOPs).
- Preparing project-specific Request for Proposals (RFPs) for analytical services.
- Providing technical and QA/QC oversight for various industrial clients.
- Training and managing data review staff.

CREDENTIALS

M.S., Organic Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania, January 1991.

B.A., Chemistry, Gettysburg College, Gettysburg, Pennsylvania, May 1989.

Radiological, Inorganic, Volatile/Semivolatile and Pesticide/PCB Data Verification and Validation Training, Lockheed Martin Energy Systems, Inc. Environmental Restoration Data Quality Program, April 1996.

SUMMARY OF EXPERIENCE

Ms. Clark has seven years of analytical/quality assurance experience. As a senior quality assurance chemist, Ms. Clark manages various projects and staff within the Valley Forge, Pennsylvania, office. Ms. Clark is knowledgeable in the fields of organic and inorganic data validation, laboratory auditing, preparing and third-party reviewing SOPs and QAPjPs, preparing analytical laboratory RFPs and reviewing laboratory proposals, and the training of quality assurance chemists.

Prior to joining Environmental Standards, Ms. Clark worked as a research chemist and a graduate teaching assistant at the University of Pennsylvania. Ms. Clark's research efforts were directed toward the total synthesis of detoxin D_1 which allowed her to develop skills in spectroscopic and separation techniques (^{1}H-NMR, IR, flash column chromatography). As a teaching assistant, Ms. Clark was responsible for overseeing organic laboratory experiments in a classroom environment and grading laboratory experiment reports and examinations. Ms. Clark also performed undergraduate research which involved the synthesis of novel facially-capping ligands in order to prepare models for the binuclear iron Purple Acid Phosphatase. As part of this research, Ms. Clark developed skills in spectroscopic techniques (^{1}H- and ^{13}C-NMR, FT-IR, GC/MS).

KEY PROJECTS

- Performed analytical data validation for numerous site investigations to determine analytical data outliers and data quality/usability. Data reviewed include those for US EPA Contract Laboratory Program (CLP) protocols, SW-846 Methods, Methods for the Chemical Analysis of Water and Wastes, and the US EPA Series 200, 500, and 600 methods.

KEY PROJECTS (Cont.)

- As part of data validation support for a site investigation, observed unusually high levels of interferences in standard ICP metals analyses. Advised the client to have the laboratory confirm some of the metal results by ICP/MS. The ICP/MS methodology was chosen for the confirmational analysis because it is not subject to the same interferences, as the ICP analysis is qualitatively very specific and generally more sensitive than the standard ICP analysis. The ICP/MS results generally supported the ICP results with a few notable exceptions. A concentration range for these exceptions was determined based on the two analyses.

- Data validation project manager for many major US EPA Region I, Region II, Region III, Region V, and NYSDEC site investigations. Project management duties include logging in and tracking data, providing technical assistance in data validation problems, reviewing quality assurance reports, tracking budgets for data package review, and providing technical assistance to clients. At times, project management has included advising laboratories on data deliverables prior to the investigation start, direct feedback to the laboratories to correct reporting errors and to improve on-going analytical work, and arranging for laboratory data deliverables to be generated after significant time lapses from when the analyses were performed. Project Management has also included providing advice to engineering contractors on data quality concerns. Provided recommendations for sample bottleware preservation, technical holding times, shipment and field quality control measures. Coordinated shipments of bottleware and environmental samples between the laboratory and the field and provided corrective action recommendations for any problems which arose.

- Managed several data validation projects for large New York State Superfund site investigations. Projects involved the full validation of data from over 1000 samples collected from the sites. Samples were contaminated with complex mixtures of Aroclors 1248, 1254, and/or 1260. Utilized in-house tools for PCB data validation so that a consistent approach to the qualitative identifications and quantitation of results could be used with all sample analyses. One project used a modification of a NYSDEC Superfund Method for the analysis for PCBs. Also advised the laboratory on improvements to the method for future analytical work for this project.

- Provided project management for an on-going data validation project for a drum disposal site. For this project, several analytical methods were required for each class of analytes due to the various levels of contamination at the site. Data examined included data for highly contaminated samples which caused many unique analytical problems. Provided significant chemistry consultation to the client regarding data validation, analytical, and database reporting issues.

- Assisted in project management and served as data validation task manager for an on-going quality assurance/quality control technical oversight project for large aircraft manufacturer. Prepared SOPs for laboratory audits, analytical work, data validation of analytical work, preparation of analytical data packages, and preparation of quality assurance reports for this extensive site investigation. In preparing the SOPs, coordination with several analytical laboratories, the data management contractor, and the client was essential. Subsequent data validation was performed for several phases of the investigation according to the requirements of data validation SOPs which included a data quality assessment and a compliance evaluation based on the analytical SOPs. Extensive coordination with the data management contractor was required throughout the validation efforts in order to identify problems in the database and to update the database remotely.

- At the request of a client, reviewed data validation reports prepared by a competitor on herbicide and pesticide/PCB analytical data for a wetlands site investigation. Identified major qualitative and quantitative laboratory errors which were missed by the competitor. The qualitative errors had a major impact on the risk assessment for the site investigation. The discovery of the errors resulted in major changes by the laboratory in its approach to the analysis for pesticides/PCBs.

- Performed laboratory audits for several major companies to assess laboratory quality and reliability. As requested by the client, the audits evaluated laboratory personnel's use of good laboratory practices, laboratory quality control/quality assurance programs, and analytical methods.

- Performed audit of an on-site industrial laboratory with the primary function of providing analytical support for procedures involved in decommissioning electrical transformers and various other electrical equipment. The laboratory analyzed dielectric oil from the equipment in order to determine if (and at what concentration) PCBs were present based on US EPA guidelines. These analyses were used to categorize equipment for disposal. In addition, the facility collected and analyzed wipe samples from the surface area of scrap parts to ensure low levels of residual PCBs. Prepared audit report summarizing findings and key recommendations for the client to improve the qualitative and quantitative QA/QC for the analyses performed.

- Has prepared and third-party reviewed several project-specific QAPjPs, which included the participation in the formulation of project strategy and Data Quality Objectives (DQOs) for submission to federal and state regulatory agencies. Has addressed comments provided by agencies on QAPjP concerns. Has provided project-specific justification for project reporting limits which did not meet regulatory agency requirements. Has also reviewed and revised Sampling and Analysis Plans.

- Provided consultation on identifying analytical alternatives to potentially expensive state requirements for analytical work for a site investigation directed by the Virginia Department of Environmental Quality. The state was requiring the use of numerous analytical methods for the analysis of only a few classes of analytes. Developed a multi-tiered decision-tree approach which provided a dramatically less expensive alternative that met the data quality objectives of the project and that overlapped with some of the requirements of the coinciding RCRA facility investigation. Also modified the QAPjP for the RCRA facility investigation to include the alternative analytical approach.

- Prepared appendices for use in a corporate environmental contract laboratory program as a guideline for the use of the corporate environmental contract laboratory program: Laboratory Specifications Manual and Analytical Services and Quality Assurance Guidance Manual, specifically for waste characterization as it relates to hazardous waste management under the Resource Conservation and Recovery Act (RCRA).

- Prepared the RFP of analytical services for a monitoring program for a major company. The RFP addressed issues including budget, personnel, experience, instrumentation, and laboratory quality control/quality assurance programs. Reviewed proposals submitted by the laboratories in response to the RFP to determine the most qualified applicant. Reviewed and aided in re-writing the project-specific laboratory quality assurance project plan prepared by the contract laboratory.

- Performed a scientific evaluation of the results from the analyses of fly ash samples in an attempt to identify the possible sources of waste materials at a landfill. The evaluation included determining which analytes should be considered indigenous to the landfill, grouping these analytes based on chemical structure and industrial processes, and comparing the groupings and individual compounds to the manufacturing processes used by various local industries.

- Prepared and issued a one-page survey to the clients of a laboratory in order to evaluate the laboratory's performance in the opinion of their clients. The survey responses were compiled and evaluated in order to determine specific areas in which the laboratory could ultimately improve their services to their clients.

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PUBLICATION

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PRESENTATION/PAPER

Clark, M. A. and M. J. Piccone. "Regional Variations in the Evaluations of Analytical Data." SUPERFUND XV. Washington, DC, 29 November-1 December 1994.

ENVIRONMENTAL
STANDARDS

RUTH L. FORMAN

Senior Quality Assurance Chemist III

FIELDS OF COMPETENCE

- Analytical and sampling quality assurance procedures.
- Analytical database design.
- Corporate laboratory program design, execution, and maintenance.
- Field operations audits.
- Laboratory auditing.
- Performance evaluations, study design, and executions.
- Project-specific analytical requests for proposal preparation.
- Project-specific quality assurance oversight.
- Quality Assurance Project Plan preparation and third-party review.
- Rigorous third-party data validation for RI/FS, RFIs/CMS, and CAA stack tests.
- Sampling and analysis plan preparation and review.
- Technical liaison among laboratories, industries, and consultants.
- Theoretical and practical knowledge of the facets of quantitative analysis for organic and inorganic pollutants by published methodologies.
- Training and managing data validation staff.

CREDENTIALS

B.A. Chemistry, Franklin and Marshall College, Lancaster, Pennsylvania, 1986.

PROFESSIONAL AFFILIATION

Air and Waste Management Association

Society of Women Environmental Professionals

SUMMARY OF EXPERIENCE

Ms. Forman has ten years of field and analytical/quality assurance experience. As a Senior Quality Assurance Chemist III, Ms. Forman manages various projects and staff within the Valley Forge, Pennsylvania, office. Ms. Forman is knowledgeable in the fields of organic and inorganic data validation (including specialty analyses), laboratory auditing, field auditing, and the preparation of third-party review of analytical standard operating procedures (SOPs), field operation SOPs, project Quality Assurance Project Plans (QAPjPs), and Request for Proposals (RFPs).

Prior to joining Environmental Standards, Ms Forman was a chemist with a primary US EPA Superfund contractor for US EPA Region III. During her tenure at this position, Ms. Forman was responsible for developing and maintaining the office quality assurance program, performing field audits, writing field SOPs, performing data validation, and managing various preliminary assessment site investigations and hazardous ranking system projects.

KEY PROJECTS

- Performed analytical data validation for numerous site investigations to determine analytical data outliers and data quality/usability. Data reviewed included those for US EPA Contract Laboratory Program (CLP) protocols, SW-846 Methods, Methods for the Chemical Analysis of Water and Wastes, and the US EPA Series 200, 500, and 600 Methods.

- Provided data validation project management for several major US EPA Region I, Region II, Region III, Region IV, and Region V site investigations. Duties included performing data log-in and providing tracking, technical assistance in data validation problems, reviewing quality assurance reports, tracking budgets for data package review, and providing technical assistance to clients.

- Conducted single-blind and double-blind performance evaluation (PE) studies for several corporate laboratory programs. The studies involved procuring the PE samples, coordinating with laboratory and/or field personnel, and evaluating the results.

- Developed and participated in national and international corporate laboratory programs for several pharmaceuticals and corporations. The development of the programs required assessing the company's current laboratory use and expenditure performing laboratory audits, conducting PE studies, preparing RFPs, evaluating proposals, ranking laboratory performance and pricing, and preparing corporation laboratory manuals.

- Performed laboratory audits for several major companies to assess laboratory quality and reliability. The audits were based upon issues of good laboratory practices, laboratory quality control/quality assurance programs, and the analytical methods requested by the client.

- Performed field audits for several major clients to assess sampling, packing and shipping techniques. Audits were based upon acceptable sampling procedures and project sampling plans.

- Provided project management for quality assurance/quality control (QA/QC) technical oversight of a three-year study (primarily air) of a large metropolitan publicly owned treatment works (POTW). Responsibilities included participating in local community committee meetings and public meetings; commenting on project activities; preparing an RFP; reviewing proposals, QAPjPs, risk assessment work plans, final reports, and analytical methods; auditing laboratories; submitting blind PE samples; conducting field audits; collecting split samples; and validating and senior reviewing all project data.

- Provided project management for a large pipeline company in the eastern United States. Responsibilities included auditing several large environmental laboratories, validating and senior reviewing project data, tracking project activity and budget status, coordinating field auditing activities, conducting round robins of multi-laboratory blind PE samples, providing technical assistance on laboratory, field, and overall project quality assurance issues.

PUBLICATION

Baldwin, J. E., T. C. Barden, R. L. Pugh-Forman, and W. C. Widdison. "Partial Loss of Deuterium Label in Wilkinson's Catalyst Promoted Decarbonylations of Deuterioaldehydes." Journal of Organic Chemistry 52 (1987):3303.

PRESENTATIONS/PAPERS

Forman, R. L., R. J. Vitale, D. C. Nuber, and D. P. Callaghan. "A Case Study: Effective Assessment of Data Usability During a Multi-Year Air Study." 91st Annual Air and Waste Management Association Meeting. San Diego, CA, 14-18 June 1998.

Mussoline, G. R., R. L. Forman, and D. P. Callaghan. "Data Management - Effective and Cost Efficient Use in an Environmental Investigation." SUPERFUND XVI. Washington, DC, 6-8 November 1995

Forman, R. L. "Quality Assurance/Quality Control at POTW." Eleventh Annual Waste Testing and Quality Assurance Symposium. Washington, DC, 23-28 July 1995

Forman R. L. "Continuous Emission Monitoring QAPPs." Delaware Valley Chapter of MASS-AWMA, Implementation of New Jersey's Title V and Enhanced Monitoring Workshop. Cherry Hill, NJ, 25-26 May 1995.

Forman, R. L. "Guidance for Determining Data Usability of Volatile Organic Compounds in Air." SUPERFUND XV. Washington, DC. 29 November-1 December 1994.

Forman, R. L., and D. C. Nuber. "Emissions Sampling - Controlling the Cost Through Data

Validation." First North American Conference & Exhibition on Emerging Clean Air Technologies and Business Opportunities. Toronto, Ontario, Canada, 26-30 September 1994.

DONALD J. LANCASTER

Senior Quality Assurance Chemist II

FIELDS OF COMPETENCE

- Analytical and environmental chemistry.
- Analytical methods development and specification design.
- Performance evaluation study design and execution.
- Project-specific analytical request for proposal preparation.
- Project-specific quality assurance oversight.
- Quality Assurance Project Plan preparation and third-party review.
- Rigorous third-party data validation RI/FS, RFIs/CMS, Permit B, and delisting studies.
- Training data validation staff.
- Laboratory audits.

CREDENTIALS

B.S., Chemistry, Minor in Mathematics, University of Arizona, Tucson, Arizona, May 1986.

Additional course work towards an M.A. Degree in Mathematics, West Chester University, West Chester, Pennsylvania.

SUMMARY OF EXPERIENCE

Mr. Lancaster has eleven years of experience in analytical chemistry and quality assurance. Specifically, he has nine years of experience in the data validation of organic and inorganic analyses, and two years of experience in the analysis of air and water samples for metals and wet chemistry parameters. As a Senior Quality Assurance Chemist II at Environmental Standards, Mr. Lancaster is involved in the quality assurance review of organic (volatile, semivolatile, pesticide/PCB, herbicides, and dioxin/furan) analyses by a variety of methods, including gas chromatography (GC), GC/mass spectroscopy (MS), high performance liquid chromatography (HPLC), and High Resolution GC/MS. Mr. Lancaster also routinely performs data validation for inorganic analyses, including metals by inductively coupled plasma (ICP), ICP-MS and graphite furnace atomic absorption (GFAA), and wet chemistry parameters by colorimetric, ultraviolet-visible (UV-VIS), ion selective electrode (ISE), and titrimetric methods. In addition, Mr. Lancaster has performed method reviews for an SW-846 Workgroup, and has written and reviewed project-specific analytical methods and data validation standard operating procedures (SOPs).

Other projects performed by Mr. Lancaster at Environmental Standards include the preparation of Requests for Proposals (RFPs) for analytical services for major US Corporations and reviews of the proposals submitted in response, and laboratory audits to assess the technical, quality assurance, and support services for major environmental laboratories in the US. Finally, Mr. Lancaster is responsible for the creation and revision of data validation SOPs used internally at Environmental Standards.

Prior to joining Environmental Standards, Mr. Lancaster was a Data Validation Chemist with a large government consulting firm in Wayne, Pennsylvania. His primary responsibilities included the data validation and the preparation of quality assurance reports for Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) site inspections performed in US EPA Region III. The analytical data reviewed included those generated by GC/MS, GC, ICP, and GFAA for the analysis of solid and aqueous samples for the Target Compound List (TCL) volatiles, semivolatiles, pesticides/PCBs,

dioxins and furans, metals and cyanide from all laboratories participating in the Contract Laboratory Program (CLP). Prior to this, Mr. Lancaster was a Research Chemist for the University Analytical Center at the University of Arizona in Tucson, Arizona. His primary responsibility was the analysis of aqueous and air filter samples for metals by ICP, flame AA, and GFAA. He also performed the analysis of aqueous and air filter samples for fluoride, chloride, bromide, nitrate, and sulfate by IC and for phosphates by UV-VIS, and the analysis of air filter samples for total hydrogen, total carbon, and total nitrogen.

KEY PROJECTS

- Performed analytical data validation for numerous site investigations to determine analytical data outliers and data quality/usability. Data reviewed included those for US EPA CLP protocols, SW-846 Methods, Methods for the Chemical Analysis of Water and Wastes, and the US EPA Series 200 and 600 methods.

- Data validation project manager for several major US EPA and NJDEPE site investigations. Duties included logging in and tracking data, providing technical assistance in data validation problems, reviewing quality assurance reports, tracking budgets for data package review and providing technical assistance to clients.

- Revised laboratory analytical manual for a site laboratory for a Fortune 500 company. The manual emphasized the importance of performing quality control analyses to assure the validity of analytical results and of documenting laboratory sample and quality control analysis results.

- Performed laboratory audits for several major companies to assess laboratory quality and reliability. The audits evaluated the laboratory's adherence to good laboratory practices, laboratory quality assurance/quality control (QA/QC) programs, and the analytical methods requested by the client.

- Performed field audits for several major clients to assess sampling, packing, and shipping techniques. The audits evaluated field personnel's adherence to acceptable sampling procedures and project sampling plans.

- Reviewed methods as part of the SW-846 Inorganic Workgroup. Methods were reviewed for technical merit and completeness. Analyses covered by methods were ignitability of solids (Method 1030), corrosivity (Method 1120), acid digestion of sediments, sludges and soils (Method 3050B), microwave-assisted acid digestion of ash and other siliceous wastes (Method 3052), and white phosphorus by solvent extraction and gas chromatography (Method 7580), all of which will be included in the Third Update for SW-846.

- Performed statistical analysis of data for a major company to show that treated wastes should not be considered hazardous and detected levels fall within US EPA-specified limits. Statistical analysis was performed in accordance with the US EPA documents "Soil Sampling Quality Assurance User's Guide" (May, 1984) and "Supplement Guidance to RAGS: Calculating the Concentration Term" (May, 1992).

- Prepared Quality Assurance Project Plan (QAPjP) for the sampling, analysis, and report distribution for the monitoring discharges and on-site wells for a Fortune 500 company. The QAPjP emphasized the documentation of all activities and stressed the importance of QA/QC.

- Prepared a number of comprehensive RFPs for analytical services for a wide variety of large short- and long-term environmental investigations. Evaluated laboratory proposals, performed laboratory audits, provided recommendations for award, and participated in contract negotiations. One such project saved a Fortune 500 company 30% in analytical costs over two years

STEPHEN T. ZEINER, CPC

Senior Quality Assurance Chemist II

FIELDS OF COMPETENCE

- Analytical and environmental chemistry.
- Analytical method specification design.
- Corporate laboratory program design, execution, and maintenance.
- Laboratory audits.
- Performance evaluation study design and execution.
- Project-specific analytical/sampling request for proposal preparation.
- Project-specific quality assurance oversight.
- Purge and trap/GC instrumentation repair and troubleshooting.
- Quality Assurance Project Plan preparation and third-party review.
- Rigorous third-party data validation RI/FS, RFIs/CMS, Permit B, delisting studies, and CAA stack tests.
- Technical liaison among laboratories, industries, and consultants.
- Technical support for laboratories.
- Theoretical and practical knowledge of all facets of quantitative analysis for organic and inorganic pollutants by published methodologies.
- Volatile organic analyses using SW-846 8000 Series and US EPA 500 and 600 Series Methods.

CREDENTIALS

B.S., Chemistry, Shippensburg University, Pennsylvania, 1988.

Shippensburg University, Pennsylvania. Graduate Analytical Chemistry Course Work.

CERTIFICATIONS

Certified Professional Chemist (CPC) – American Institute of Chemists, Alexandria, Virginia.

Member – American Institute of Chemists (MAIC) – American Institute of Chemists, Alexandria, Virginia.

PROFESSIONAL AFFILIATIONS

American Association for the Advancement of Science – Member
American Chemical Society – Member
American Institute of Chemists – Member
Society of Environmental Management and Technology – Member

SUMMARY OF EXPERIENCE

Mr. Zeiner has seven years of analytical and quality assurance experience. Specifically, he has two years of analytical experience performing analyses for organic contaminants in a variety of media by instrumental methods, including research and development of analytical methodologies. As a Senior Quality Assurance Chemist II, Mr. Zeiner has five years of experience in the fields of organic, inorganic, radiological, and wet chemistry data validation (including specialty analyses such as dioxin/furan data); laboratory audits/evaluations, third-party review and production of Quality Assurance Project Plans (QAPjPs) for remedial investigations/feasibility studies (RI/FS), a

Resource Conservation and Recovery Act (RCRA) Facility Investigation/corrective action plan (RFI/CAP) and remedial actions; design of specialty analytical data package deliverables to accommodate project-specific data quality objectives (DQOs); specification of quality assurance/quality control (QA/QC) parameters for investigative sampling events; third-party review and critique of laboratory standard operating procedures (SOPs); management of several chemists on large data validation and corporate contract laboratory programs; project cost tracking; review of project invoices; production and evaluation of cost proposals; and design of corporate contract laboratory programs.

Prior to employment at Environmental Standards, Mr. Zeiner was a Chemist I for a large independent analytical laboratory. He was responsible for performing volatile organic analyses by SW-846 and US EPA 500 and 600 Series Methods using purge and trap gas chromatography (GC) with photoionization (PID), flame ionization (FID), and electrolyte conductivity (ELCD) detectors. His responsibilities included writing laboratory-specific modifications of SW-846 and US EPA methods, writing and updating SOPs, designing and implementing a comprehensive repair and preventive maintenance program, and training sixteen chemists in the repair and performance of preventive maintenance procedures for purge and trap/GCs. In addition, he researched and developed a laboratory method for the application of purge and trap/GC techniques for separation and detection of non-halogenated/non-aromatic volatile organic compounds.

KEY PROJECTS

- Performed analytical data validation for numerous site investigations to determine analytical data outliers and data quality/usability. Data was reviewed according to US EPA Contract Laboratory Program (CLP) protocols; SW-846 Methods; Methods for the Chemical Analysis of Water and Wastes; and the US EPA Series 200, 500, and 600 Methods.

- Served as data validation project manager for US EPA Region II and NYSDEC site investigations. Duties included data log-in and tracking, assisting in technical data validation problems, reviewing quality assurance reports, tracking budgets for data package review, and providing technical assistance to clients.

- Served as project manager for the development of a corporate contract laboratory program that included a Laboratory Users/Corporate Quality Assurance Guide. Developed a written survey to collect project information from approximately 80 client sites. Designed a client-specific Request for Proposal (RFP). Additionally, laboratory audits were performed on the short-listed laboratories, and the laboratory proposals were evaluated and ranked.

- Served as part of the peer review team for the US EPA Region I organic data validation guidelines.

- Served as project manager for a preliminary NYSDEC site investigation for Aroclor characterization. Duties included the preparation of a Request for Quotation (RFQ), review and evaluation of proposals, preparation of data package deliverables that were required for the project-specific analytical protocol, and performance of a laboratory audit of the selected project laboratory.

- Served as part of a project team for the development of a Corporate Quality Assurance Program and Laboratory Users Guide. Developed a written laboratory survey aimed at determining the capabilities of a facility. Additionally, performed laboratory audits to "short-list" bid candidate laboratories.

- Served as an on-site technical consultant to three laboratories. Duties included the review of data package deliverables prior to issuance and the review of analytical data for accuracy and adherence to volatile organic, semivolatile organic, and inorganic method protocols.

- Assisted in an extensive on-site audit of a laboratory for a Fortune 100 client. Audited GC and GC/mass spectroscopy (MS) organic analyses, sample log-in and receipt, data packaging, and the reporting areas within the laboratory. Provided feedback of audit findings to the laboratory during a debriefing session. Prepared a detailed audit report summarizing audit findings.

- Served as part of a project team for the review and comparison of US EPA stack testing methodologies and European stack testing methodologies for polychlorinated dibenzodioxin/polychlorinated dibenzofuran (PCDD/PCDF) parameters. Duties included the review and comparison of the analytical procedures and QC requirements for the US EPA and European methodologies.

- Served as an analyst for purge and trap/GC analyses by US EPA 500 and 600 Series Methods and SW-846 Methods. In addition, served as a troubleshooting and repair person for sixteen purge and trap/GC instruments. Duties included repair, analysis, maintenance, and research and development for volatile organic purge and trap/GC analyses.

- Provided data validation services for an RFI at a major aircraft corporation. Reviewed PCDD/PCDF, volatile, semivolatile, and pesticide/PCB compounds for several data package delivery groups. Prepared reports and performed secondary review of reports and data tables for several additional packages.

- Developed an RFQ that included the analytical specifications and QA/QC procedures necessary for laboratories to perform work and accurately bid work under the client's environmental contract laboratory program. The laboratories were also requested to provide additional technical information for review by Environmental Standards.

- Co-authored and managed the development of an Environmental Contract Laboratory Program – Analytical Services and Quality Assurance Guidance Manual, which include information useful both to the client's staff for project planning and to the laboratory's staff for sample analysis and data package generation. Topics in the manual included analytical methods, data package specifications, communication schemes, DQO options, QA/QC procedures, corrective actions, and electronic deliverable specifications.

- Served as part of a team that audited and evaluated several laboratories' sample log-in and receipt procedures, organization, sample preparation methods, analytical expertise and compliance, QA/QC procedures, documentation procedures, data packaging procedures, and results reporting methods. Co-authored detailed audit reports that included descriptions of the laboratories' procedures. A ranking report based on the technical aspects evaluated during the audits was provided to the client.

- Served as a project manager and as technical support to a Fortune 100 industrial client for a US EPA Region II RI/FS. Served as contact point for technical questions regarding data quality issues, as well as managing chemists performing data validation on solid and aqueous samples.

PUBLICATION

Zeiner, S. T. "HazWaste World/SUPERFUND XVII." The Chemist Vol. 73, No. 6 (Nov./Dec. 1996).

PRESENTATION/PAPER

Zeiner, S. T. "Realistic Criteria for the Evaluation of Field Duplicate Sample Results." SUPERFUND XV. Washington, DC. 29 November-1 December 1994.

CONFERENCE MODERATOR/CHAIR

Zeiner, S. T. Chairperson. "Brownfields: State and Local Lessons." HazWaste World/SUPERFUND XVIII. Sheraton Washington Hotel, Washington, DC, 2-4 December 1997.